RENU · JAIN
S3b.

Chemical Principles
and
Inorganic Chemistry

Fundamental Inorganic Chemistry

(A Modern Approach)

Hybrid Orbitals

sp^3 HYBRID

sp^2 HYBRID + p_z ORBITAL

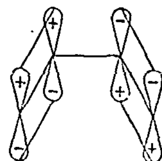
sp HYBRID + p_y AND p_z ORBITALS

The three important hybrids of 2s and 2p orbitals. Only the sp^3 hybrids are used in saturated molecules; the sp^2 hybrids are found in alkenes and sp hybrids in alkynes.

Chemical Principles and Inorganic Chemistry

A Textbook for H. S., Pre-University, Pre-Medical, Pre-Engineering, and Intermediate Students

Fundamental Inorganic Chemistry



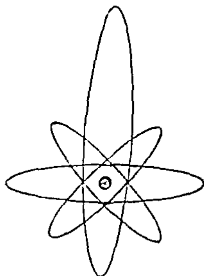
(A Modern Approach)

BY

P. L. Soni

Head of the Department of Chemistry
Hans Raj College, Delhi University, Delhi

1972
Thirteenth Edition
(*Revised & Enlarged*)



SULTAN CHAND & SONS
PUBLISHERS
4792/23, Daryaganj, Delhi-6

Some Useful Books for Hr. Sec. and Pre-University Science Students

1.	अकार्बनिक रसायन, (सातवां संस्करण, 1972) कार्ड कवर	Rs. 11'00
	प्रो० एल० सोनी (क्लोथ बाउन्ड)	Rs. 12'50
2.	Principles of Chemistry *(Soft cover)*	Rs. 8'50
	by P. L. Soni *(Hard cover)*	Rs. 9'20
3.	Fundamental Inorganic Chemistry *by* P. L. Soni (12*th Edition*, 1971)	Rs. 11'00
4.	कार्बनिक रसायन—डा० सत्यकुमार	Rs. 6'50
5.	कार्बनिक रसायन—सत्यकुमार व सरभाई (1971)	Rs. 4'00
6.	Fundamental Organic Chemistry *by* P. L. Soni (10*th Edition*, 1971)	Rs. 7'50
7.	Prelude to Organic Chemistry *by* Dr. J. L. Norula (2*nd Ed.*	Rs. 4'50
8.	प्रयोगात्मक रसायन—सोनी 2nd *Edn.* 1972	Rs. 5'00
9.	Fundamental Practical Chemistry *by P. L. Soni (7th Revised Edn. 1971)*	Rs. 4'50
10.	रासायनिक गणनाएँ—सरीन व सत्यकुमार (3 *Ed.* 1971)	Rs. 3'75
11.	रसायन की भाषा—सरीन व सत्यकुमार	Rs. 1'25
12.	Numerical Problems in Chemistry *by* Sarin & Sarin *(Tenth Edn.* 1972)	Rs. 5'00
13.	Language of Chemistry *by* Sarin & Sarin (Third Ed.)	Rs. 1'25
14.	Catalysed Chemistry (Ques. Ans.) *by Singhal & Rajendra*	Rs 15'00
	Vol. I Rs. 6'00 Vol. IIA Rs. 3'00 Vol. IIB	Rs. 6'00
15.	Applied Chemistry *by Mrs. K. Kapoor*	Rs. 2'50
16.	माध्यमिक भौतिक विज्ञान —ए. एन. पुरी व डॉ० एन. पी. गुप्ता (1970)	Rs. 16'50
17.	प्रारम्भिक भौतिक शास्त्र— *A. N. Puri*	Rs. 6'00
18.	An Elementary Course of Physics *by A. N. Puri*	Rs. 10'00
19.	Higher Secondary Practical Physics *by A. N. Puri* (10th Edition)	Rs. 5'00
20	Viva-Voce in Physics *by K. L. Puri & Sukhbir Singh*	Rs. 4'00
21.	Numerical Problems in Physics *by B. L. Dhar* (2nd Edition)	Rs. 6'50
22.	प्रायोगिक भौतिकी—सरभाई व मिश्रा	Rs. 7'50
23.	[illegible] *(Edition, 1971)*	Rs. 12'00

To
Chemists of
Tomorrow

Preface

Inorganic Chemistry occupies a key position in the school syllabus. In view of the rapid pace with which the subject is developing, it is becoming increasingly important that its presentation should reflect the modern outlook. I have tried to achieve a balance between what must be included to meet the requirement of syllabus and the far more exciting story of recent developments. It is the latter which will capture the imagination and make the subject live.

Among the Special Features *of this revised and enlarged edition are* :

(1) There is unanimity about the importance of visual aids in the teaching of chemistry. These leave a deep impression on the young minds. The book has been profusely illustrated and the illustrations will serve as visual acids. In addition to the large number of full page illustrations, every chapter begins with an illustration.

(2) Every effort has been made to include up-to-date factual material, for example, latest figures of capacity and production of various chemical industries in India have been given. Elements with atomic numbers 104 (Kurchatovium, Ku) and 105 (Hahnium, Ha) have been discovered recently. Another element at. no. 112 (Eka-mercury) has been reported. All these have been included in the Periodic Table.

(3) Concept of chemical affinity as cause of chemical action is misleading. Modern chemists explain it on the basis of energy changes. Latest concepts of Enthalpy, Entropy and Free Energy changes have been used while explaining the cause of chemical action on page 1·25.

(4) Collision theory of chemical reaction has been discussed on page 1·29.

(5) Shapes of molecules explained with the help of different models on page 1·36.

(6) Properties of Gases discussed in terms of Particle model for gases on page 1·99.

(7) Mole concept discussed on page 1·116.

(8) Some modern concepts about solutions—Why substances dissolve ?—Why does a substance have different solubilities in different solvents ?—are given on page 1·193.

(9) Products of Electrolysis have been explained in the light of Preferential Discharge Theory and Discharge Potentials on page 1·202.

(10) Mechanism of catalysis given in terms of Activation energy and Reactivity of adsorbed molecules (page 1·247).

(11) Idea of Heat Content or Enthalpy explained in a newly added chapter—Energy Changes in Chemical Reactions, page 1·253.

(12) Effort has been made, wherever possible, to interpret and explain the descriptive chemistry in the light of modern physical concepts. For example :

(*i*) Difference between solids, liquids and gases has been explained in terms of positions and energies of molecules, page 1·18.

(*ii*) Properties of water and hydrofluoric acid have been explained in light of hydrogen bonding, pages 2·30 and 2·88.

(*iii*) Various changes observed on heating of sulphur are explained in terms of the nature of the structure of chains of its molecules, page 2·118.

(*iv*) Preparation of Heavy water in terms of Isotope effect, page 2·11.

(13) Scale models have been added to give an idea of the shape and size of some molecules.

(14) Modern chemists explain the structure of very large number of compounds using the concepts of Hybridization and Resonance. These have been treated in very simple language in the Chapter "Theory of Chemical Bonding" which forms a separate chapter (chapter 10) and includes Hydrogen Bonding and van der Waals Attraction. I am confident the students will grasp these without any difficulty.

(15) Chapter on Periodic Classification of Elements has been rewritten. Long form of the table has been discussed at length. Modern concepts like those of Ionization potential, Electron affinity and Eleotronegativity have been explained in very simple language.

(16) The concepts of Oxidation numbers—Oxidation and Reduction in terms of change in oxidation numbers—Definition of Acids as Proton donors and Bases as Proton acceptors—Hydronium ion—Shells and sub-shells—Orbitals—Formation of a covalent bond by overlap of orbitals, given in the form of an appendix in the previous edition have been incorporated at appropriate places in the text.

(17) Separate sections are given on :

(i) Kinetic Theory of Gases (page 1·108).

(ii) Process of Dissolution and concentration of solutions in terms of Molarity, Formality, Normality, Molality, Mole fraction.

(iii) Nuclear Stability (page 1·78).

(iv) Detection of Isotopes (page 1 83).

(18) Concept of Activity Series to explain whether a suggested reaction will occur or not, has been introduced in Oxidation and Reduction. Terms like Electronation and de-electronation used in modern textbooks have been explained here.

(19) Physical properties of metals have been explained in terms of strength of metal bonding on page 2·283.

(20) An appendix is given on Ionic Equations and Ion-electron method of balancing Ionic equations.

(21) Flow charts for the manufacture of aluminium at Alwaye (Kerala) and steel at Rourkela will be found interesting.

I dedicate this book to the Chemists of Tomorrow and I *believe that* those who use it will find not only a fascinating account of what has been achieved but also a stimulus to help in solving many problems which remain.

My warmest thanks are due to several teachers and students of chemistry all over India, for their suggestions, criticism and appreciation for this book. I have every hope that the present edition will be found more useful.

24·7·72 P. L. SONI

Contents

PART I—CHEMICAL PRINCIPLES

PART II—INORGANIC CHEMISTRY

Appendix

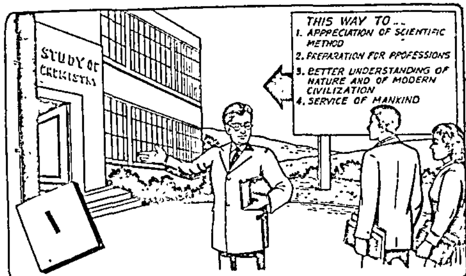
PART I

CHEMICAL PRINCIPLES

(A Modern Version of Various Concepts)

"The beauty and mystery of our world intrigues the mind of the curious, and presents a challenge to the adventurous, and a great adventure of today is to be found on the frontiers of science."

—*STANLEY BE-*



Science and Scientific Method

1. What is Science? Man's curiosity is proverbial and ever since the dawn of civilization, he has been trying to understand the changes going on in the world around him. He has been constantly receiving a great number of impressions through his senses of hearing, sight, smell, taste and touch. He has further been trying to correlate various natural phenomena and has found in them an inexhaustible and endless chain of cause and effect. Thus he has accumulated an immense storehouse of knowledge which extends over the entire realm of nature. *This systematised store of human knowledge gained after generalising and interrelating the various isolated facts is termed* Science.

Properly speaking the term science deals with observation and interpretation of *reproducible facts*. The reproducibility is both qualitative and quantitative. Thus a liquid always flows from a higher level to a lower level. Twelve grams of carbon will always burn in excess of air to produce forty-four grams of carbon dioxide. Study of these facts of nature is covered by *natural sciences*.

2. The Scientific Method.—To satisfy his curiosity about a certain phenomenon, a scientist tries to collect maximum possible number of relevant facts about that phenomenon. These facts are collected through careful observation under controlled conditions or otherwise. Observation under controlled conditions is essential to achieve the aims of science. *A controlled sequence of observations is called* [illegible]

Basic activities of Science

1 *To accumulate information through observation*

2 *To organise this information and to seek regularities in it*

3 *To wonder why the regularities exist.*

4. *To communicate the findings to others*

in performing experiments under controlled and reproducible conditions and to make careful and detailed observations. The scientist then tries to discover any regularities in these observations. The search may lead to wrong conclusions as sufficient observations may not have been made. Yet there is no other way to advance than by such a step though it may be only a leap in the dark.

After the scientist has made a list of the regularities in the observations from a set of controlled experiments, he tries to seek an explanation for these (wondering why !). To arrive at the explanation he may have to perform more experiments and may come across some other unexplained regularities. The quest for knowledge never ends—experiments leading to more experiments.

Consider our observations about burning of objects. We find from a large number of observations that air is essential for burning of objects. Then we perform experiments to see which part of air is necessary for combustion. Again our experiments lead us to the conclusion that oxygen is essential for combustion. We perform more experiments and find that sodium will burn in an atmosphere of chlorine. So we find that after all, oxygen is not essential for combustion. Then we try to find out regularities, if any, between burning of carbon in oxygen and of sodium in chlorine. Thus our search continues as experiments performed to explain certain phenomena may bring to light some other unexplained observations.

For the progress of science it is essential that results of controlled experiments and conclusions drawn therefrom are communicated to others. If it were not so, the same experiments may have to be repeated by different workers from time to time (and may be at the same time, if they are unaware of each other's pursuit) to rediscover the same regularities. Thus if Boyle's work had not been communicated to others we would have to perform experiments on pressure-volume changes in gases to come to the same conclusions. This effort would have been wasted. As it is, the results are available to us through published works—a large number of journals in each country are helping in making known to others the scientific work being carried out in different laboratories.

3. Natural Laws, Hypotheses and Theories.—When a number of regularities of natural phenomena or experimental facts have been observed, these are put forward as general statements known as Laws, e.g., Newton's Laws of Motion, and Boyle's Law. *A Law or a Natural Law is simply a description of the uniform behaviour of nature.*

When a number of inter-related laws have been discovered, a scientist tries to find something common among them (*regularity* in the laws). He tries to visualise a picture of nature which can be explained on the *collective basis* of the above laws. Such



a **model** *i.e., mental picture or set of assumptions, concerning the nature and structure of some portion of the universe is called a* **hypothesis.** Thus from various gas laws scientists concluded that gases consist of discrete moving particles and the *kinetic-molecular hypothesis* was put forward.

As a result of the statement of a hypothesis, new lines of investigations may be indicated. The experiments performed may lead to the discovery of new regularities and new natural laws.

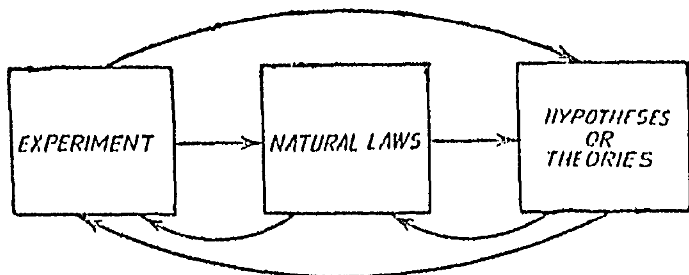


Fig. 1·1.

Once a hypothesis has been tested by a variety of experiments and has been found to be in accord with our existing knowledge of the subject, it becomes a *theory*. *A theory correlates and explains the known facts.* In addition, it is useful in making predictions also. More experiments are performed to test these predictions giving rise to new hypotheses and theories, and so on.

4. **What is Chemistry ?**—We see a variety of changes going on around us. Wood burns and ash is left behind. Milk sours to give curd. Cane juice, when allowed to stand, yields vinegar. Iron rusts in moist air. In each case a new substance is obtained with properties entirely different from those of the original substance. Changes of this kind are termed **chemical changes.** *The branch of science, which deals with chemical changes around us and the conditions which influence these changes, is termed* **chemistry.** *It also includes the study of composition and properties of various substances.*

5. **Development of Chemistry.**—Chemistry in its crude form studied long ago as "black art" was called *Alchemy*. Having its birthplace in Egypt, alchemy was introduced into Europe by the Arabs. It was not a study of chemistry for its own sake. It was rather a search for three interesting things, *viz.*,

(i) *Philosopher's stone* which would convert all baser metals, *e.g.*, iron, copper, into gold just by rubbing. The alchemists believed that God had created all metals in the form of gold, a part of which changed into baser metals owing to some defect. Consequently, the transmutation of baser metals into gold was considered possible after removing the defect.

(ii) *The Universal solvent* which would dissolve anything and everything. Probably they never thought how they would store it if it was actually found.

(iii) *The Elixir of life* which would cure diseases and prolong the span of life to a very great degree.

The era of modern chemistry began with the work of such men as Priestley, Scheele and Lavoisier who organised the jumbled facts which the alchemists had found. It was in the days of Boyle that a study of chemistry began for its own sake. He is, therefore, called the "Father of Chemistry". *Lavoisier introduced the use* of balance into the study of chemistry. He tried to interpret in a scientific way the jumble of facts collected by the alchemists. He is, therefore, considered as the "Founder of Modern Chemistry".

In India, long, long ago, our forefathers knew the art of extraction of metals from their ores, manufacture of drugs, dyes and *fermentation products*. Ashoka's *iron pillar of* rustless steel near the Qutab in Delhi speaks of the perfection we had attained in the art of metallurgy. The *Somaras* (सोमरस) of the Aryans and the *Tari* (ताड़ी) of the Dravidians were certainly fermented liquors. Kanada's view on the structure of matter that it was made up of tiny and unchangeable particles, *Paramanu* (परमाणु), is only the central idea of our Modern Atomic Theory.

6. **Different Branches of Chemistry.**—For the sake of convenience, chemistry has been sub-divided into different branches. The boundaries of these branches are not very rigid and many scientists work on the borders. It is rather difficult at times to say whether an investigator is a biochemist or an organic chemist, an industrial chemist or an inorganic chemist. The various branches are :

(i) *Inorganic Chemistry*. It is the branch concerned largely with inanimate objects of physical universe.

(ii) *Organic Chemistry*. It is the branch dealing with compounds of carbon, majority of them having a vegetable or animal origin.

(iii) *Physical Chemistry*. The branch dealing with the explanation of fundamental principles underlying various chemical phenomena is called Physical Chemistry. Laws and theories of chemistry and the like fall within the domain of this branch.

(iv) *Industrial Chemistry*. The branch dealing with chemistry in relation to industry is termed Industrial Chemistry.

(v) *Analytical Chemistry*. This is the branch dealing with the detection and estimation of elements and compounds.

(vi) *Biochemistry*. It is the branch dealing with chemical changes going on in the body of the living things—animals and plants.

7. **Importance of Chemistry in Everyday Life.**—If you look around you will find that chemistry plays a very significant role in almost all walks of life. It influences every part of our daily life. From morning till night we use chemical products and perform chemical reactions.

We drink water which has been chemically purified, while bathing we clean our body with soap, a chemical product. We wear clothes which were bleached or dyed with chemicals. Various articles of food are products of chemical industries. Digestion itself is largely a chemical process.

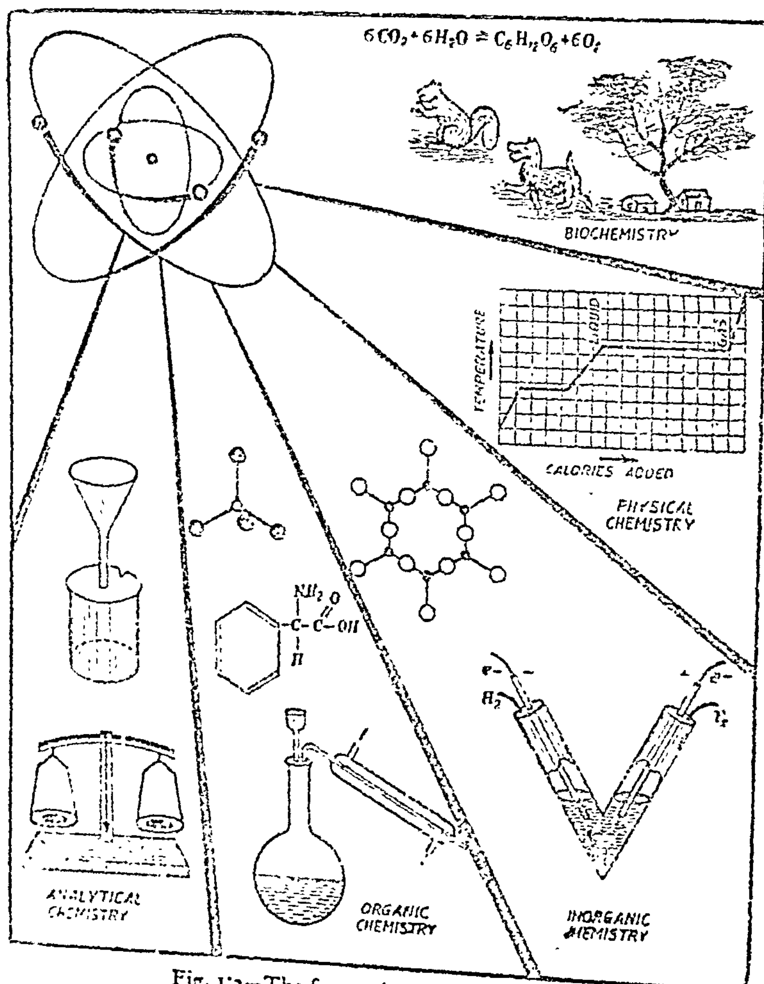


Fig. 1·2—The five major fields of chemistry.

Some major contributions of chemistry to life in the modern world are :

(1) **Its contribution to improve health.** Modern chemical discoveries have done a lot to eradicate disease and improve health. Some important contributions are :

(i) *Anaesthetics and antiseptics.* Discovery of anaesthetics and antiseptics has gone a long way in saving millions of lives. It made serious operations possible as they could now be carried out painlessly and without fear of the wound getting 'septic'—poisoned in any way.

(ii) *Disinfectants and Germicides.* The use of disinfectants and germicides helps us to prevent spread of diseases.

(iii) *Drugs and Antibiotics.* Discovery of sulpha drugs and penicillin made pneumonia a curable disease. *Antibiotics* like streptomycin, aureomycin and chloromycetin have enabled us to cure T.B. and so many other ailments. Almost every day chemists are creating new and better drugs. A few latest are *psychochemicals* (*Reserpine* and *Frenquel*) used in treating mental diseases.

(iv) *Prophylactics.* Use of prophylactics (disease preventing serums and vaccines) has made epidemics like plague, smallpox and cholera things of the past. Some latest prophylactics are *Salk vaccine* employed in the fight against polio and *Cytillen* for treatment of diseases of the circulatory system.

(2) **Supply of foodstuffs.** We look to the chemist for help to solve our acute food shortage by scientific agriculture. His chief contributions in this field are :

(i) *Fertilizers.* He is responsible for the fertilizers which enrich our soil. Plants need mainly nitrogen, phosphorus and potassium for their growth. Chemical compounds containing these elements are added to the soil and keep it fertile.

(ii) *Insecticides.* We are grateful to the chemist for the insecticides we spray on plants to save them from being eaten away or spoilt by various insects. Our problem is not only to produce more foodstuffs but also to preserve them. Large quantities of these get damaged while in storage or in transit Introduction of powerful insecticides like D.D.T. and methoxychlor has rendered the storage of grains safer.

(iii) *Preservation.* Fruits and vegetables which could not be kept for even a few days can now be preserved and used after months. These are all applications of chemistry.

(iv) *Balanced diet.* It is as a result of our study of chemistry that we realise the importance of balanced diet—a diet containing suitable quantity of various food essentials.

(v) *Preventing Adulteration.* A chemist is toiling in the laboratory testing our foodstuffs for adulterants and improving them.

(3) Increase in comfort, convenience and pleasure. In every walk of life the chemist has been the pioneer contributor towards the happiness of man. He has helped us in getting a number of amentities. For example :

(*i*) *Domestic requirements.* We look up to him for most of our domestic requirements, *e.g.*, paper, fabrics (rayon, nylon, etc.), soaps, cosmetics, oils, flavouring essences, dyes and perfumes.

(*ii*) *Rendering travel safe and convenient.* On the road we depend upon him for high-grade motor fuels. High speed machinery, the locomotives and the aeroplanes, constantly at work in the service of man are all an outcome of the labour of a chemist in extraction of pure metals from their ores more particularly in the preparation of alloys such as alloy-steels (used in locomotives) and duralumin (used in the manufacture of aeroplanes).

(*iii*) *Air-conditioning.* To keep efficient in all seasons we make use of air-conditioning. In this we use chemical substances like liquid ammonia or liquid sulphur dioxide.

(4) The increased efficiency of industrial processes. Prosperity of a nation depends on the extent of its industrialisation and the richer a nation, the more civilized it is known to be. We all look to chemist for the development of our various chemical industries, *e.g.*, paper, sugar, starch, vegetable oils, vegetable ghee, essential oils, tannery, distillery, heavy chemicals and metallurgy.

(5) Chemistry and War. Chemistry has increased the striking power of man by providing explosives such as T.N.T., poisonous gases, incendiary bombs, and other deadly weapons. Today's most horrible weapons of destruction, the atomic and hydrogen bombs, are the recent achievements of chemistry.

Simply because the chemist helps us in preparing explosives and poison gases, it will be unjust on our part to accuse him of fostering warfare. If some war-mongers exploit these products for the destruction of mankind, the chemist is not to be condemned. These very explosives and poison gases could be put to numerous uses in the service of mankind, such as mining of ores, blasting of rocks and killing certain enemies of man such us locusts.

QUESTIONS

Essay-type Questions

1. What is Science ? What do you understand by scientific method ?
2. What are laws, hypotheses and theories ?
3. What are the reasons for you to believe that chemistry is an important branch of science ?
4. Write an essay on the following :

"Whether chemistry is a blessing or a curse for the man, depends on its use." Explain giving examples.

5. (a) What do you understand by chemistry ? Name various branches of chemistry.

(b) Write an interesting essay on Role of Chemistry in Modern Life. (*Punjab H.S. 1965*)

6. Write a note on "Role of chemistry in agriculture." (*Punjab Pre-University 1971*)

Test Your Understanding

7. Which of the following statements are correct ? Correct the statements which you feel incorrect.

(i) The scientific observations are not reproducible.

(ii) Science deals with observation and interpretation of irreproducible facts.

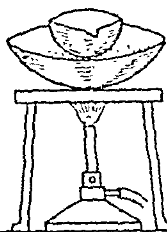
(iii) The aim of science is to satisfy the inherent curiosity of a person.

(iv) A controlled sequence of observations is called an experiment.

(v) Mathematical way of representing a regularity is the worst way of doing so in chemistry.

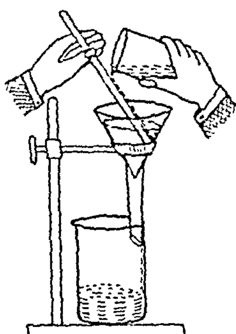
(vi) A natural law is simply a description of the uniform behaviour of nature.

INSIDE A LABORATORY

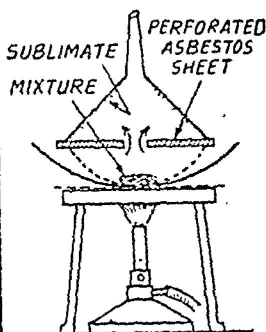


EVAPORATION

2



FILTRATION



SUBLIMATION

Simple Laboratory Processes

1. **Solution.**—When we add a spoonful of sugar to some water in a cup, the sugar gradually disappears. Sugar is said to have dissolved in the water. A teaspoonful of sugared water from the top of the cup is as sweet as a teaspoonful from the middle or bottom of the cup. This shows that sugar dissolves in water to form a homogeneous mixture in which the quantity of sugar to be added can be varied within certain limits. *The homogeneous mixture of sugar and water so obtained is termed a* **solution.**

The substance which dissolves is termed *solute* and the other substance in which the solute dissolves is called *solvent*. For example, in the above case sugar is the solute and water is the solvent.

2. **Unsaturated and Saturated Solutions.**—When a cube of sugar is added to a cup of tea, it dissolves. If this process of addition of sugar cubes is continued, a limit is reached when the last sugar cube does not dissolve. *The solution so obtained in which no more sugar can be made to dissolve, except by raising the temperature, is called a* **saturated solution.**

Previous to this stage of saturation when the solution could dissolve more and more of the solute, it was an unsaturated solution. *An* **unsaturated solution** *is one that can dissolve more of the solute at that temperature.*

3. **Decantation.**—Take some muddy water in a beaker and allow it to stand for some time. We notice that suspended particles of clay and sand settle at the bottom with clear water above. *The process of setting of suspended particles is called* **s[illegible]mentation.** The process of sedimentation can b[illegible]lerated b[illegible]ng some alum. The clear water at the top c[illegible]y po[illegible]ther beaker. *The process of separatio*[illegible] *liquid in this manner is termed* d[illegible]

4. **Filtration.**—Separation of an insoluble substance from a liquid is not complete by decantation. Separation is therefore, effected by *filtration. It is the process of removing an insoluble substance from a liquid by allowing it to pass through a porous material, e.g.,* a layer of sand or a filter paper. A filter paper is folded twice and then opened out in the form of a cone and is fitted into a glass funnel (Fig. 2·1).

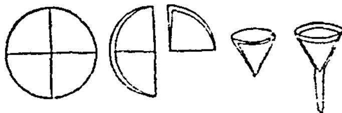


Fig. 2·1—How to fold a filter paper.

This cone is moistened a little to enable it to stick to the surface of the glass funnel. The liquid is next decanted on to the cone with the help of a glass rod (Fig. 2·2) The clear liquid passes through the filter paper and collects in the flask below. It is called the *filtrate.* The insoluble substance left behind in the beaker or on the filter paper is called the *residue.*

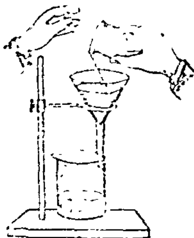


Fig. 2·2—Decantation and filtration.

In industry, filtration is done *through big canvas filters. Purification of river water for drinking is carried on by filtration through sand beds.*

5. **Evaporation.**—When a solution is heated in a dish, water escapes in the form of steam leaving the solid salt behind in the dish. The process is called *evaporation.* Slow evaporation is going on at all temperatures. Ponds get dried up in summer due to slow evaporation of water. On heating the solution, the evaporation is rapid. The solution is heated in the laboratory on a sand bath or a water bath.

Common salt is prepared from sea water by evaporation. Sea water is run into shallow ponds and allowed to stand. Water evaporates slowly and common salt is deposited.

6. **Crystallization.**—On allowing the hot saturated solution of a solid to cool, the solid separates in the form of particles *having regular geometrical shapes.*

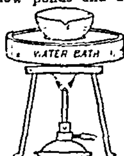


Fig 2 3—Heating on a sand bath.



Fig. 2 4—Heating on a water bath

These particles are termed crystals. For example, alum forms eight-sided or *octahedral* crystals and copper sulphate deposits *rhombohedral* crystals that are blue in colour. *The process of deposition of crystals of a salt from its saturated solution is called* **crystallization.** Chemists purify chemicals by crystallization.

7. **Distillation.**—Impure liquids are purified in the laboratory by distillation.

The impure liquid is evaporated and the vapours thus obtained are cooled when they condense to give pure liquid. *The process in which evaporation and condensation are going on side by side is called* **distillation.**

Apparatus used in the laboratory for distillation is shown in Fig. 2·5. Some salt solution is placed in the distillation flask fitted

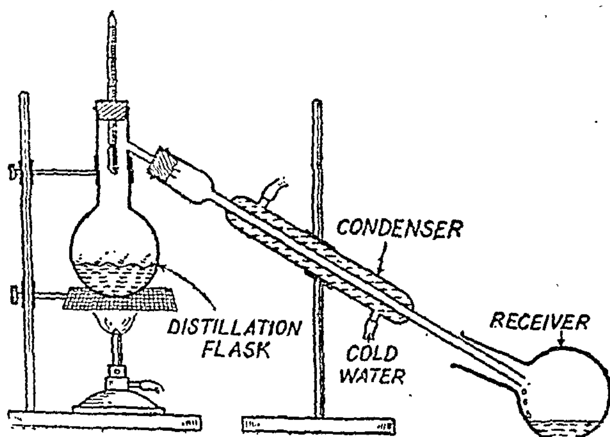


Fig. 2·5—Distillation.

with a thermometer and a Liebig's condenser. The distillation flask is heated and cold water is circulated through the condenser. Water in the distillation flask evaporates and the vapours condense while passing through the condenser to give pure water which collects in the receiver.

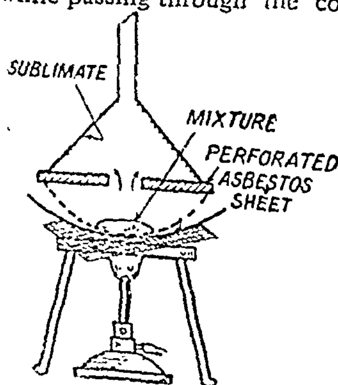
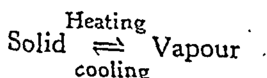


Fig. 2·6—Sublimation.

8. **Sublimation.**—Certain substances pass directly from solid to vapour state on heating and *vice versa* on cooling, *e.g.*, ammonium chloride, naphthalene, comphor and indigo.



$$\text{Solid} \underset{\text{cooling}}{\overset{\text{Heating}}{\rightleftharpoons}} \text{Vapour}$$

The process is known as sublimation and is found very useful in separating substances which sublime on heating from non-volatile ones or *vice versa.*

... with a per- ... is placed (Fig. ... on the cooler walls of the funnel.

9. **Precipitation.**—Take some common salt solution in a *test tube and add silver nitrate solution to it. A white substance* appears in the test tube. The insoluble substance so obtained is called a precipitate and the process of getting a precipitate is called *Precipitation*. A precipitate obtained can be separated by filtration.

Experiment. Add some barium chloride to dilute sulphuric acid and filter the white precipitate thus obtained.

QUESTIONS

Essay-type Questions

1. Explain the meaning of the following terms :

(*a*) Solution, (*b*) Sublimation, (*c*) Distillation, (*d*) Crystallisation, (*e*) Decantation. (*Punjab H.S.* 1964, 62 ; *Bihar* 1963, 62 ; *Delhi* 1969)

2. What is a saturated solution ? What happens when a hot saturated solution of nitre is allowed to cool ?

Test Your Understanding

3. Fill in the blanks in the following .

(*i*) Homogeneous mixture of sugar and water is termed... Sugar is termed.. .. whereas water is called . .

(*ii*) Solution in which no more solute can dissolve except by raising the temperature is a/an . solution

(*iii*) The process of settling of suspended particles is called . ..

(*iv*) The process of separation of an insoluble substance from a liquid by settling the suspended particles and pouring gently the clean liquid at the top is termed . .

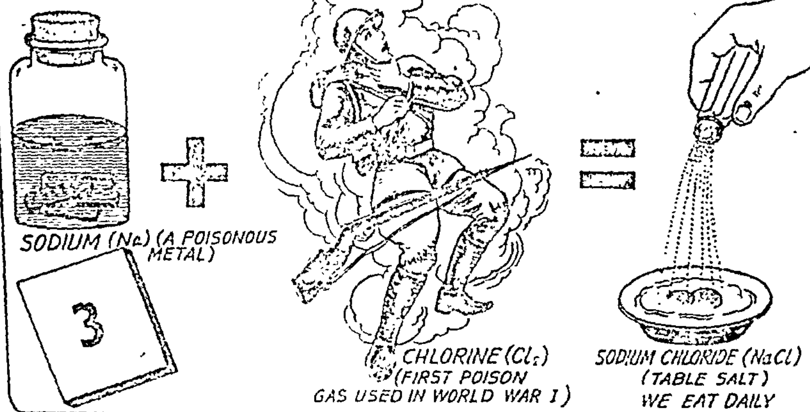
(*v*) The process of deposition of crystals of a salt from its solution is called .....

(*vi*) The process in which and are going on side by side is known as distillation.

(*vii*) Passing directly from solid to vapour state on heating and *vice versa* on cooling is termed . .

KEY

(*i*) Solution, solute, solvent, (*ii*) saturated, (*iii*) sedimentation, (*iv*) decantation, (*v*) saturated, crystallisation, (*vi*) evaporation, condensation, (*vii*) sublimation.



Elements, Compounds and Mixtures

1. **Matter.**—We see a number of things around us, *e.g.*, wood, iron, water, etc. We do not see air but we feel its presence. All these things occupy space and have weight. *Anything which occupies space and has weight is called* matter.

In spite of the fact that all things occupy space and have weight, they are not similar.

(*i*) Ice, iron, wood, etc., have a definite volume and definite shape. These are **solids.**

(*ii*) Water, milk, oil, etc., have a definite volume but no shape. These always assume the shape of the container. These are called **liquids.**

(*iii*) Air, steam and hydrogen have neither a definite volume nor definite shape of their own. These are termed **gases.**

Thus we find that matter exists in three states, *viz.*, solid, liquid and gaseous. The same substance can exist in three states. For example, at room temperature water is in liquid state. On

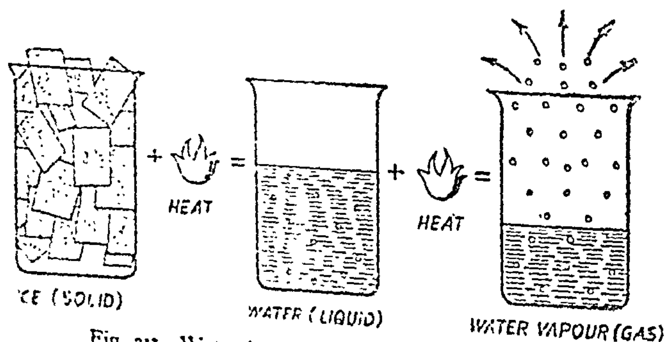


Fig. 3·1—Water in three different states of matter.

cooling it solidifies and gives ice. When heated it changes into water vapour. Ice (solid), water (liquid) and water vapour (gas) are three states of the same substance.

2. **Element.**—Various substances which we come across in the world are classified as elements, compounds and mixtures. *Simple forms of matter which cannot be decomposed into simpler substances are called* **elements**. Sulphur, iron, lead, mercury and hydrogen are examples of elements. We cannot decompose sulphur and prepare new substances.

There are 106 elements known at present. Their relative abundance in nature whether occurring free or in the combined state has been diagrammatically shown in Fig. 3·2.

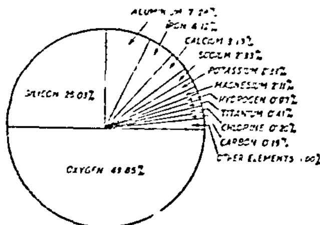


Fig. 3·2—Relative abundance of various elements in nature.

3. **Atom.**—*The smallest particle of an element which may or may not be capable of independent existence is termed an* **Atom**.

An **element** *is a pure substance that contains only one kind of atoms.*

Until recent times the atom has been thought to be an indivisible particle. As a result of the modern researches, however, atom is no longer considered to be an indivisible particle. *It is supposed to be made up of electrons, protons and neutrons.* Atoms have actually been broken by atom-smashing machines and some of them explode spontaneously.

4. **Compounds.**—On passing electric current through water, it [illegible] which are simple [illegible] of matter such [illegible] "composed of two or more ingredients."

A compound is a substance produced by union of two or more elements in a definite proportion. It can be decomposed into two or more simpler substances. Carbon dioxide, lime and washing soda are some examples of compounds.

Characteristics of a compound are :

(*i*) It is homogeneous and consists of two or more elements.

(*ii*) The elements contained are present in a definite proportion by weight.

(*iii*) Properties of a compound are different from the properties of its component elements, *e.g.*, hydrogen burns and oxygen helps burning but their compound, water, extinguishes fire.

(*iv*) A compound cannot be separated into its constituents by simple mechanical means.

(*v*) Energy in the form of heat, light, electricity, etc., is either evolved or absorbed when a chemical compound is formed.

5. **Molecule.**—*Smallest particle of an element or a compound which is capable of independent existence is called a* **molecule.** It is the smallest particle of a substance which possesses the properties of that substance. It cannot be subdivided without destroying its characteristic properties.

In case of elements if atom is capable of independent existence, then the atom is also the molecule. Molecule of a compound is made up of two or more different kinds of atoms.

All matter is composed of molecules and all molecules are made up of atoms.

6. **Atomic and Molecular Weights.**—Atoms and molecules are so small particles that their weights are inconveniently small in terms of grams, *i.e.*, gram is too big a unit to weigh an atom or a molecule. For example, the weight of a carbon atom is 0·000,000,000,000,000,000,000,0195 gm. ($1·95 \times 10^{-23}$ gm.). To overcome this difficulty, one-twelfth of the weight of a carbon atom is selected as a unit of weight for the purpose and is termed atomic mass unit (amu).

Atomic weight of an element is the average relative weight of its atom as compared with that of carbon atom (C^{12} isotope) taken as 12 amu. It is only a number. By saying that atomic weight of magnesium is 24, we only mean that an atom of magnesium is twice as heavy as an atom of carbon. *For atomic weights of commoner elements, refer to the table on page 1·32.*

Molecular weight of a substance is the relative weight of its molecule as compared with an atom of carbon taken as 12 amu. This also is only a number. By saying that molecular weight of magnesium carbonate is 84, we only mean that a molecule of magnesium carbonate is 7 times as heavy as an atom of carbon.

7. **Mixtures.**—On grinding iron filings with sulphur, a dark-coloured substance is obtained. This possesses the properties of iron filings and sulphur both. For example,

(*i*) On moving a magnet through the powder, iron filings are separated.

(ii) On adding carbon disulphide to the powder, sulphur dissolves leaving iron filings behind.

(iii) Looking under a magnifying glass, the particles of sulphur and iron can be seen lying side by side.

(iv) Iron and sulphur can be mixed in any proportion.

A jumble of two or more elements or compounds [illegible] fixed order or proportion is called a **Mixture.** For example, the dark powder mentioned above is a mixture of sulphur and iron filings. Gunpowder is a mixture of sulphur, charcoal and nitre. Similarly air is a mixture of nitrogen, oxygen, and some other gases.

Characteristics of a mixture are :

(i) Unlike compounds the ingredients of a mixture may be present in any ratio.

(ii) Their composition is not the same throughout, i.e., these are not homogeneous.

(iii) The properties of a mixture are an average of the properties of its constituents.

(iv) A mixture can be separated into its constituents by simple mechanical means.

(v) Generally no energy is evolved or absorbed when a mixture is obtained.

8. Distinction between a Chemical compound and a Mechanical mixture.—Various points of distinction between a chemical compound and a mechanical mixture are tabulated below :

Chemical Compound	Mechanical Mixture

9. Separation of Mixtures.—Various physical processe employed in the separation of mixtures are :

(i) Decantation or filtration. Solid substances suspende in a liquid can be separated by decantation or filtration (se page 1·11). For example, powdered chalk suspended in water ca be separated by filtration.

(ii) Evaporation. A solid can be separated from its solutio by evaporation (see page 1·11). For example, a solution of sulphu in carbon disulphide on evaporation yields sulphur.

(iii) Solution. The soluble constituent of a mixture i separated from the insoluble one by dissolving in a suitable solvent For example, a mixture of sand and sugar is separated by shakin with water when sugar goes in solution and sand is left behind The solution of sugar is separated from sand by filtration to dry- ness to regain sugar.

(iv) Sublimation. Certain substances which sublime on heat- ing can be separated from others by sublimation (see page 1·12). For example, from a mixture of common salt and ammonium chloride the latter sublimes on heating.

(v) Based on other properties. Sometimes one of the cons- tituents of a mixture is iron filings. This can be separated with the help of a magnet. For example, a mixture of glass-powder and iron filings can be separated by moving a magnet in the mixture.

Experiment. *To separate a mixture of glass-powder, iron filings and ammonium chloride.*

A magnet is moved into the mixture when the iron filings cling to the magnet and get separated. The residual mixture is heated as given above when ammonium chloride sublimes over leaving glass-powder behind.

(vi) Simple Distillation. Mixture of liquids which boil under ordinary pressure without decomposition and non-volatile ones are generally separated by simple distillation (see page 1·12). For example, water is freed from its non-volatile impurities by distillation. Two liquids having their boiling points far apart are also separated by distillation.

10. Atomic-Molecular Theory and Three States of Matter.— According to the atomic-molecular theory, matter is made up of molecules. Essential difference between the three states of matter is due to the state of aggregation of these molcules and the energies associated with them.

In solids the molecules are closely packed and can vibrate only to and fro about their fixed positions.

Due to the close packing of molecules the solids have a definite shape and definite volume. On account of the small to

and fro motion of their molecules, the solids are associated with minimum energy.

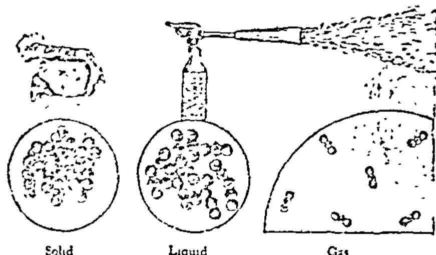


Fig 1'3—All matter consists of molecules In a gas these molecules are far apart, in a liquid or solid these are closely packed. (*A highly magnified imaginary model*).

Solids on heating melt to give liquids. Heat energy supplied during heating makes the molecules more energetic and enables them to overcome forces of mutual attraction and move away from each other. A few more energetic molecules even escape as gases. The positions of molecules are not fixed in liquids and they have, therefore, no definite shape. Their volume is, however, definite.

On heating, the liquids change into gases. Heat supplied during heating makes the molecules more energetic and they move farther away. Thus in gases the molecules are widely separated and their positions are not fixed with the result that gases have neither definite shape nor definite volume

Points of distinction between the three states of matter are summarised in the table given below

QUESTIONS

Essay-type Questions

1. (*a*) What is matter ? What do you know about three states of matter ? (*Bihar H.S. 1961 Supp.*)

(*b*) How does the particle model of matter enable us to explain the differences in solid, liquid and gaseous phase of matter ? (*Punjab Pre-University 1970*)

2. (*a*) What do you understand by an element, a mixture and a compound ? Classify the following into elements, mixtures and compounds : tin, gunpowder, common salt, blue vitriol, copper turnings and air.

(*b*) How will you distinguish between a compound and mixture ? (*Bihar H.S. 1966 ; Punjab 1963*)

3. Classify the following into elements, compounds and mixtures :

Honey	Soap	Hydrogen	Kerosene
Sugar	Nitre	Marble	Sea-water
Water	Milk	Brass	Magnesium
Air	Iron	Sulphur	Slaked lime

4. (*a*) Suggest suitable methods by which the constituents of the following mixtures can be separated ; (i) Iron filings and sand ; (ii) Ammonium chloride and Sodium chloride ; (iii) Sand and Sugar ; (*iv*) Water and Common salt ; and (*v*) Sugar and Sulphur.

(*b*) You are given a mixture of powdered glass, ammonium chloride and copper sulphate. How would you proceed to recover the various constituents from it ? Sketch the apparatus. (*Punjab H.S. 1964*)

5. Define elements and compounds giving examples.

What experiments would you perform to prove that solution of sodium chloride in water is a mixture, not a compound ? (*Bihar H.S. 1966, 61*)

Test Your Understanding

6. Tick mark against most suitable answer from the alternatives suggested in the following :

(i) (Air/copper/water) is an example of a compound.

(ii) A substance which cannot be decomposed into simpler substances is termed (element/compound/mixture).

(iii) Air is a mixture because it (1) is colourless, (2) is odourless, (3) does not have fixed composition, (4) can be liquefied.

(*iv*) In (solids/liquids/gases) molecules are closely packed, are associated with more energy and their positions are not fixed.

7. Fill in the blanks in the following :

(*i*) Anything which occupies space and has weight is called......

(ii) Forms of matter which cannot be decomposed into simpler substances are called......

(iii) The simplest particle of an element which may or may not be capable of independent existence is termed a/an......

(*iv*) A......is a substance produced by union of two or more elements in a ......proportion. It can be decomposed into two or more simpler......

(*v*) Smallest particle of an element or a compound which is capable of ...... is called a/an......

(*vi*) Atomic weight of an element is the average, relative weight of its atom as compared with that of......atom (......isotope) taken as......

(*vii*) A jumble of two or more elements or compounds in no fixed order or proportion is called a/an ......

KEY

6. (*i*) water ; (ii) element ; (iii) 3 ; (*iv*) liquids.

7. (i) matter ; (*ii*) elements ; (*iii*) atom ; (*iv*) compound, definite, substances ; (*v*) independent existence, molecule ; (*vi*) carbon, C^{12} 12 ; (*vii*) mixture.

QUESTIONS

Essay-type Questions

1. (a) What is matter ? What do you know about three states of matter ? (*Bihar H.S. 1961 Supp.*)

(b) How does the particle model of matter enable us to explain the differences in solid, liquid and gaseous phase of matter ? (*Punjab Pre-University 1970*)

2. (a) What do you understand by an element, a mixture and a compound ? Classify the following into elements, mixtures and compounds : tin, gunpowder, common salt, blue vitriol, copper turnings and air.

(b) How will you distinguish between a compound and mixture ? (*Bihar H.S. 1966 ; Punjab 1963*)

3. Classify the following into elements, compounds and mixtures :

Honey	Soap	Hydrogen	Kerosene
Sugar	Nitre	Marble	Sea-water
Water	Milk	Brass	Magnesium
Air	Iron	Sulphur	Slaked lime

4. (a) Suggest suitable methods by which the constituents of the following mixtures can be separated ; (i) Iron filings and sand ; (ii) Ammonium chloride and Sodium chloride ; (iii) Sand and Sugar ; (iv) Water and Common salt ; and (v) Sugar and Sulphur.

(b) You are given a mixture of powdered glass, ammonium chloride and copper sulphate. How would you proceed to recover the various constituents from it ? Sketch the apparatus. (*Punjab H.S. 1964*)

5. Define elements and compounds giving examples.

What experiments would you perform to prove that solution of sodium chloride in water is a mixture, not a compound ? (*Bihar H.S. 1966, 61*)

Test Your Understanding

6. Tick mark against most suitable answer from the alternatives suggested in the following :

(i) (Air/copper/water) is an example of a compound.

(ii) A substance which cannot be decomposed into simpler substances is termed (element/compound/mixture).

(iii) Air is a mixture because it (1) is colourless, (2) is odourless, (3) does not have fixed composition, (4) can be liquefied.

(iv) In (solids/liquids/gases) molecules are closely packed, are associated with more energy and their positions are not fixed.

7. Fill in the blanks in the following :

(i) Anything which occupies space and has weight is called......

(ii) Forms of matter which cannot be decomposed into simpler substances are called......

(iii) The simplest particle of an element which may or may not be capable of independent existence is termed a/an......

(iv) A......is a substance produced by union of two or more elements in a ......proportion. It can be decomposed into two or more simpler......

(v) Smallest particle of an element or a compound which is capable of ......is called a/an......

(vi) Atomic weight of an element is the average, relative weight of its atom as compared with that of an atom (C...isotope) taken as......

(vii) A jumble of two or more elements or compounds in no fixed order or proportion is called a/an......

KEY

6. (i) water ; (ii) element ; (iii) 3 ; (iv) liquids.

7. (i) matter ; (ii) elements ; (iii) atom ; (iv) compound, definite, substances : (v) independent existence, molecule ; (vi) carbon, C^{12} 12 ; (vii) mixture.

PHYSICAL CHANGES (TEMPORARY)
1. MELTING OF ICE
2. GLOWING OF LAMP
3. FRACTIONAL DISTILLATION OF LIQUID AIR

CHEMICAL CHANGES (PERMANENT)
3. ELECTROLYSIS OF WATER

4

Physical and Chemical Changes

1. Physical Change.—We see daily a variety of changes. Ice melts, water changes into steam and sugar dissolves in water. In all these changes only the physical appearance of the substance changes, the identity of the substance remains unaltered. Further, the changes are temporary and can be easily reversed. For example, water freezes to give ice and ice can be melted to obtain water. Similarly on heating [illegible] gives back water. [illegible] and we get sugar [illegible] back solid sugar. This shows that all such changes are temporary and can be reversed. Such changes are termed physical changes.

Thus a temporary change in which the identity of a substance does not change is called a Physical change.

The branch of science which deals with physical changes in matter is called Physics.

Some more examples of physical changes are :

(i) *Heating of a Platinum wire.* Heat a platinum wire in a Bunsen flame. It becomes red hot and emits light. Cool the wire and it regains its original colour. In other words, the identity of the platinum wire does not change and the change is temporary. It is, therefore, a physical change.

(ii) *Melting of sulphur.* Heat some sulphur in a dish. It melts but its identity [illegible]

a physical change.

(*iii*) *Glowing of an Electric lamp.* Switch on the current, the electric lamp begins to glow. The metal filament becomes white hot and emits light. Switch off the current, we find that the filament cools to original colour and does no more glow. This shows that during glowing of the lamp, the identity of the metal filament does not change and the change is temporary.. It is, therefore, a physical change.

(*iv*) *Magnetising an iron needle.* Rub an iron needle with a magnet, it gets magnetised and attracts iron filings. Heat the magnetised needle in flame for a few minutes and bring it near iron filings. It does not attract iron filings, *i.e.*, it is demagnetised. Magnetisation is, thus a temporary change and during magnetisation, the identity of iron needle does not change. It is, therefore, a physical change.

2. **Chemical Change.**—Milk sours, wood burns and iron rusts. In all these cases the original substance loses its identity and new substances with new properties are obtained. Further these changes are permanent and cannot be easily reversed. Such changes are called chemical changes.

Thus a permanent change in which the identity of a substance changes is called a **Chemical change.**

Some more examples of a chemical change are :

(*i*) *Burning of a candle.* A candle burns and gives carbon dioxide and water vapours. The identity of the products is entirely different from that of candle. Moreover, it is not possible to prepare a candle from the products. It is, therefore, a chemical change.

(*ii*) *Burning of magnesium ribbon.* A magnesium ribbon burns with a dazzling light and magnesium oxide (a white powder) is obtained. Identity of magnesium oxide is entirely different from that of magnesium. Moreover the change is permanent, since we cannot get back magnesium ribbon from the oxide obtained by simple means. It is, therefore, a chemical change.

(*iii*) *Burning of hydrogen.* Hydrogen combines with oxygen on burning to produce water—a substance entirely different from hydrogen. Hydrogen is combustible and oxygen helps combustion but the product, water is used in extinguishing fire. It is also a permanent change, since we cannot get back hydrogen from water by simple means. So it is a permanent change in which the identity of hydrogen is changed. It is, therefore, a chemical change.

(*iv*) *Rusting of iron.* When iron is exposed to moist air, it rusts. Rust is yellow coloured iron oxide, entirely different from iron. It is a permanent change, since we cannot get back the metal from the yellow powder by simple means. Thus rusting is a permanent change during which the identity of iron changes. It is, therefore, a chemical change.

3. Distinction between Chemical and Physical Changes.—Various points of distinction between the two types of changes are summarized in the table.

Physical Change	Chemical Change
1. Only the physical properties of the substance change and the composition remains unaltered.	1. Chemical composition of the substance is altered.
2. No new substance is obtained.	2. New substance with entirely different properties is obtained.
3. The change is temporary and can be reversed by ordinary physical means.	3. The change is permanent and is not reversed by ordinary physical means.
4. Generally energy in the form of heat, light or electricity is neither evolved nor absorbed.	4. Energy in the form of heat, light or electricity is either evolved or absorbed.

4. Some Problem Questions.—The concept of physical and chemical changes is an elementary concept which will inculcate in the beginners a faculty of observation and reasoning. It is, however, difficult to give a categorical answer sometimes. Let us take a few so-called problem questions

(i) *Dissolution of hydrogen chloride in water*. On dissolution in water gaseous hydrogen chloride gives aqueous hydrogen chloride which on heating gives back the gaseous hydrogen chloride. This is, therefore, a temporary change and the identity of the substance does not change. It is, therefore, a physical change.

Aqueous hydrogen chloride further ionizes to give hydronium ions and chloride ions which are new species with different properties. Ionization of aqueous hydrogen chloride is, therefore, a chemical change.

Thus we conclude that dissolution of hydrogen chloride in water as such is a physical change but its ionization further is a chemical change.

(ii) *Sublimation of ammonium chloride*. On heating ammonium chloride vaporises. In the vapour state it is partially dissociated into ammonia and hydrogen chloride which again recombine to give ammonium chloride. On cooling it gives back solid ammonium chloride.

It is thus a temporary change in which the identity of ammonium chloride does not change. In other words it is a physical change.

It can, however, be argued that sublimation is a combination of four changes :

(*a*) Vaporisation of solid ammonium chloride, (*b*) partial dissociation of ammonium chloride into ammonia and hydrogen

(iii) *Glowing of an Electric lamp.* Switch on the current, the electric lamp begins to glow. The metal filament becomes white hot and emits light. Switch off the current, we find that the filament cools to original colour and does no more glow. This shows that during glowing of the lamp, the identity of the metal filament does not change and the change is temporary.. It is, therefore, a physical change.

(iv) *Magnetising an iron needle.* Rub an iron needle with a magnet, it gets magnetised and attracts iron filings. Heat the magnetised needle in flame for a few minutes and bring it near iron filings. It does not attract iron filings, *i.e.*, it is demagnetised. Magnetisation is, thus a temporary change and during magnetisation, the identity of iron needle does not change. It is, therefore, a physical change.

2. **Chemical Change.**—Milk sours, wood burns and iron rusts. In all these cases the original substance loses its identity and new substances with new properties are obtained. Further these changes are permanent and cannot be easily reversed. Such changes are called chemical changes.

Thus a permanent change in which the identity of a substance changes is called a **Chemical change.**

Some more examples of a chemical change are :

(i) *Burning of a candle.* A candle burns and gives carbon dioxide and water vapours. The identity of the products is entirely different from that of candle. Moreover, it is not possible to prepare a candle from the products. It is, therefore, a chemical change.

(ii) *Burning of magnesium ribbon.* A magnesium ribbon burns with a dazzling light and magnesium oxide (a white powder) is obtained. Identity of magnesium oxide is entirely different from that of magnesium. Moreover the change is permanent, since we cannot get back magnesium ribbon from the oxide obtained by simple means. It is, therefore, a chemical change.

(iii) *Burning of hydrogen.* Hydrogen combines with oxygen on burning to produce water—a substance entirely different from hydrogen. Hydrogen is combustible and oxygen helps combustion but the product, water is used in extinguishing fire. It is also a permanent change, since we cannot get back hydrogen from water by simple means. So it is a permanent change in which the identity of hydrogen is changed. It is, therefore, a chemical change.

(iv) *Rusting of iron.* When iron is exposed to moist air, it rusts. Rust is yellow coloured iron oxide, entirely different from iron. It is a permanent change, since we cannot get back the metal from the yellow powder by simple means. Thus rusting is a permanent change during which the identity of iron changes. It is, therefore, a chemical change.

3. Distinction between Chemical and Physical Changes.—Various points of distinction between the two types of changes are summarized in the table.

Physical Change	Chemical Change
1. Only the physical properties of the substance change and the composition remains unaltered	1. Chemical composition of the substance is altered
2. No new substance is obtained	2. New substance with entirely different properties is obtained.
3. The change is temporary and can be reversed by ordinary physical means	3. The change is permanent and is not reversed by ordinary physical means
4. Generally energy in the form of heat, light or electricity is neither evolved nor absorbed	4. Energy in the form of heat, light or electricity is either evolved or absorbed

4. Some Problem Questions.—The concept of physical and chemical changes is an elementary concept which will inculcate in the beginners a faculty of observation and reasoning. It is, however, difficult to give a categorical answer sometimes. Let us take a few so-called problem questions.

(i) *Dissolution of hydrogen chloride in water.* On dissolution in water gaseous hydrogen chloride gives aqueous hydrogen chloride which on heating gives back the gaseous hydrogen chloride. This is, therefore, a temporary change and the identity of the substance does not change. It is, therefore, a physical change.

Aqueous hydrogen chloride further ionizes to give hydronium ions and chloride ions which are new species with different properties. Ionization of aqueous hydrogen chloride is, therefore, a chemical change.

Thus we conclude that dissolution of hydrogen chloride in water as such is a physical change but its ionization further is a chemical change.

(ii) *Sublimation of ammonium chloride.* On heating ammonium chloride vaporises In the vapour state it is partially dissociated into ammonia and hydrogen chloride which again recombine to give ammonium chloride. On cooling it gives back solid ammonium chloride.

It is thus a temporary change in which the identity of ammonium chloride does not change. In other words it is a physical change.

It can, however, be argued that sublimation is a combination of four changes :

(a) Vaporization of solid ammonium chloride, (b) partial dissociation of ammonium chloride into ammonia and hy

chloride, (*c*) recombination of ammonia and hydrogen chloride to give back ammonium chloride, (*d*) solidification of ammonium chloride vapours. Out of these (*a*) and (*d*) are physical changes while (*b*) and (*c*) are chemical changes. Of course the change on the whole is a physical change.

5. Chemical Action.—*Whenevre a chemical change occurs, a chemical reaction is said to have taken place.*

Different modes of Chemical Action are :

(i) Chemical Union. *It is the combination of simple substances to form more complex ones.* For example, magnesium burns in oxygen to give magnesium oxide.

MAGNESIUM + OXYGEN → MAGNESIUM OXIDE

Similarly, hydrogen burns in the atmosphere of chlorine to give hydrochloric acid.

HYDROGEN + CHLORINE → HYDROCHLORIC ACID

(ii) Decomposition. *It is the breaking down of complex substances into simpler ones.* For example, mercuric oxide decomposes on heating into mercury and oxygen.

MERCURIC OXIDE → MERCURY + OXYGEN

Similarly, water decomposes on passing electric current through it into hydrogen and oxygen.

WATER → HYDROGEN + OXYGEN

(iii) Displacement. *It is a change in which one element enters a compound in place of another, the latter being set free.*

For example, zinc displaces hydrogen from hydrochloric acid.

ZINC + HYDROCHLORIC ACID → ZINC CHLORIDE + HYDROGEN

Similarly, iron displaces copper when placed in copper sulphate solution.

IRON + COPPER SULPHATE → COPPER + IRON SULPHATE

(iv) Double Decomposition. *It is an exchange of corresponding parts between two compounds* and takes place usually in aqueous solution. Precipitation of silver chloride on adding silver nitrate to any soluble chloride or precipitation of barium sulphate by adding barium chloride to any soluble sulphate are examples of double decomposition.

SODIUM|CHLORIDE + SILVER|NITRATE → SILVER CHLORIDE + SODIUM NITRATE
(sodium chloride: *soluble*; silver nitrate: *soluble*; silver chloride: *insoluble (white ppt.)*)

POTASSIUM|SULPHATE + BARIUM|CHLORIDE → BARIUM SULPHATE + POTASSIUM CHLORIDE
(potassium sulphate: *soluble*; barium chloride: *soluble*; barium sulphate: *insoluble (white ppt.)*)

(v) Isomeric Change. *It is an internal re-arrangement of atoms.* For example, different atoms present re-arrange themselves to give urea (an organic compound) when ammonium cyanate is heated.

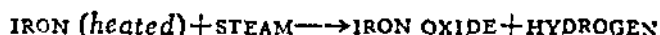

AMMONIUM CYANATE ⟶ UREA*

6. Energy.—Energy is defined as the ability to do work. Various forms of energy usually encountered in chemistry are potential energy, kinetic energy, heat energy, electrical energy and chemical energy.

Potential energy refers to energy possessed by a body by virtue of its position and kinetic energy is the energy possessed by it because of its motion. *Water in a dam possesses potential* energy and as it flows down through a pipe, the potential energy changes into kinetic energy. This falling water is made to turn the blades of a turbine which converts the kinetic energy into electrical energy.

Chemical energy is the potential energy stored in elements or compounds that can be released during a chemical reaction or a physical transformation. The chemical energy required or generated may be in the form of either heat or electrical energy. *A reaction which occurs with the evolution of heat is exothermic while another reaction in which energy is required is endothermic.*

7. Cause of Chemical Action.—A chemical reaction proceeds due to some sort of chemical attraction called chemical affinity between various atoms. For example,


IRON (*heated*) + STEAM ⟶ IRON OXIDE + HYDROGEN

In the above reaction iron is said to have greater affinity for oxygen than hydrogen. Hence it is able to snatch the element of oxygen from hydrogen in water, forming iron oxide and liberating hydrogen.

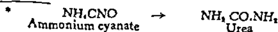
When hydrogen is blown over heated iron oxide, we get back iron and steam.


IRON OXIDE (*heated*) + HYDROGEN ⟶ IRON + STEAM

This is explained by saying that hydrogen has greater affinity for oxygen than iron and hence is able to snatch the element of oxygen from iron and produce water.

Thus we make two contradictory statements in explaining a *reversible reaction* (*i.e.*, a reaction which can proceed forward and backward depending upon conditions). The concept is obsolete and no longer used.

Modern chemists explain the cause of a chemical action on the basis of energy changes. It is a matter of common experience


* NH_4CNO (Ammonium cyanate) → $NH_2CO.NH_2$ (Urea)

that all natural systems tend to lose potential energy and become more stable. For example water stored in an overhead tank has more potential energy than water on the ground. If there is no obstruction water will always flow from the tank to the ground (more stable position), losing potential energy in doing so.

Analogous to the 'stored potential energy' of a mechanical system, each substance has some stored free energy symbolized by G. In a chemical reaction the system always loses free energy, *i.e.*, a chemical reaction occurs because of the inherent tendency of a chemical system to decrease free energy and pass on to a more stable system.

Free energy depends upon the following two factors:

(i) The heat content of the system termed as enthalpy and symbolized by H. Every system tends to decrease its enthalpy by losing heat energy.

(ii) The randomness termed as entropy and symbolized by S.

A system with high value of heat content is unstable and tends to lose heat energy spontaneously or under conducive conditions. Most reactions which form stable compounds, liberate energy. The energy liberated or absorbed in a physical or chemical process is called *enthalpy change* symbolized by ΔH which is the difference between the enthalpy of the final state, H_f and the enthalpy of the initial state, H_i.

$$\Delta H = H_f - H_i$$

By definition, ΔH is negative when energy is liberated.

As a result of the second inherent tendency, the particles tend to occupy as much of the available space as possible and thus assume a state of maximum disorder or randomness. This increase in randomness is a measure of increase in entropy symbolized by ΔS.

Why wood burns ? This is because burning releases energy and increases randomness (Products occupy larger volume), *i.e.*, since the enthalpy of the system decreases and the entropy increases. As a result of these changes a less stable system changes into a more stable system.

In some cases the two effects of enthalpy and entropy may oppose each other and still lead to a net change. When elements combine to form a compound which is more ordered, the entropy decreases but the energy released i.e., decrease in enthalpy overweighs the entropy effect and the combination is possible.

ΔS is measured in calories per degree (absolute) while both ΔH and ΔG values are given in calories. Hence in the equation, connecting ΔS, ΔG and ΔH, the ΔS values must occur multiplied by the absolute temperature T at which the reaction takes place so that all the quantities are expressed in calories. The equation connecting these is

$$\Delta G = \Delta H - T.\ \Delta S.$$

When heat is evolved, ΔH is negative and when there is increase in entropy ΔS is positive. Applying these conclusions to the equation above, we see that a reaction is theoretically possible when ΔG is negative. In endothermic reactions (heat absorbed, ΔH positive), the overall value of ΔG may be negative, if there is a large increase in entropy in the reaction.

Following examples will illustrate the influence of these factors :

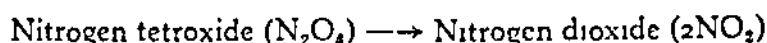
(i) In the reaction



Hydrogen+Oxygen→Water

ΔH is $-68·3$ kcal. When the gases combine to give liquid water, randomness or entropy decreases and $T\Delta S=+11·6$ kcal (a minor factor). ΔG, therefore, remains negative ($=-56·7$ kcal) and the reaction is possible.

(ii) In the reaction



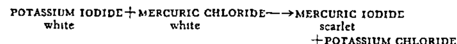
Nitrogen tetroxide (N_2O_4) ⟶ Nitrogen dioxide ($2NO_2$)

heat is absorbed *i.e.*, ΔH is positive However, entropy increases as one mole of N_2O_4 decomposes to give 2 moles of NO_2. This increase in entropy is sufficient to keep ΔG negative and the reaction is possible.

8. **Conditions which favour a Chemical Action.**—Different chemical reactions proceed differently under different conditions. Some of the conditions which favour a chemical action in general are :

(i) Contact. Before a chemical action takes place between two substances, these must be brought in intimate contact with each other. *The closer the contact, the better the chemical reaction.*

Expt. 1 Mix some potassium iodide crystals (white) and mercuric chloride (white) in a mortar. The mixture is practically white in colour. Now rub it with a pestle, it acquires a reddish colour which deepens on further rubbing By rubbing we bring the reactants into an intimate contact which favours the chemical reaction resulting in the formation of more and more mercuric iodide, scarlet in colour.



POTASSIUM IODIDE+MERCURIC CHLORIDE⟶MERCURIC IODIDE
white white scarlet
+POTASSIUM CHLORIDE

Expt 2 Put a few drops of hydrochloric acid on some washing soda placed on a piece of paper Strong effervescence occurs only when the two come in contact, with the evolution of carbon dioxide.

(ii) Solution Chemical reaction proceeds in some cases only when solutions of the reactants are mixed together

Expt. 3 Mix some oxalic acid crystals with sodium carbonate. No reaction takes place even when the mixture is rubbed in a pestle and mortar. Now add some water to the mixture, a strong effervescence occurs with the evolution of carbon dioxide.

decrease in energy between initial and final states, but because of the high activation energy required, reaction (*a*) is much slower than reaction (*b*).

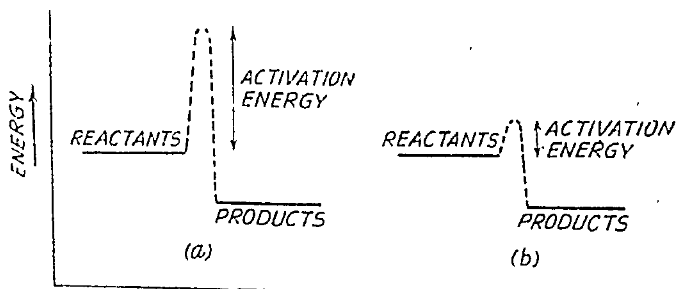


Fig. 4·2—Activation energy. (*a*) large. (*b*) small.

Thus we note that—

1. *The possibility of a reaction taking place depends on* ΔG *values (see page* 1·27)

2. *The speed of a reaction taking place depends on the value of activation energy.*

A reaction which may be thought possible (ΔG being negative), cannot always be effected, since the speed of the reaction may be infinitesimally small.

QUESTIONS

Essay Type Questions :

1. What are the principal characteristics of a chemical change and how is it distinguised from a physical change ? Illustrate your answer with examples of both types of changes.

Are the following changes physical or chemical :

(i) Burning of candle ; (ii) Preparation of sulphur crystals ;
(iii) Preparation of soap from oil and caustic soda ;
(iv) Ripening of fruit ; (v) Dissolving of NaCl in water.

(*Delhi H.S. 1970, 68 ; Bihar 1965 ; Punjab 1962*)

2. Are the following changes physical or chemical ? Explain giving reasons in each case :

(*a*) Burning of charcoal ; (*b*) Rusting of iron ;
(*c*) Passing carbon dioxide through lime water ;
(*d*) Mixing sugar with tea ; (*e*) Bursting of water pipes in winter ;
(*f*) Electrolysis of water ; (*g*) Heating copper sulphate crystals ;
(*h*) Burning of cow-dung ;
(*i*) Conversion of rhombic sulphur into monoclinic sulphur ;
(*j*) Solution of hydrogen chloride gas in water ;
(*k*) Fractional distillation of liquid air ;
(*l*) Melting of ice cream ; and (*m*) Radioactivity of uranium.

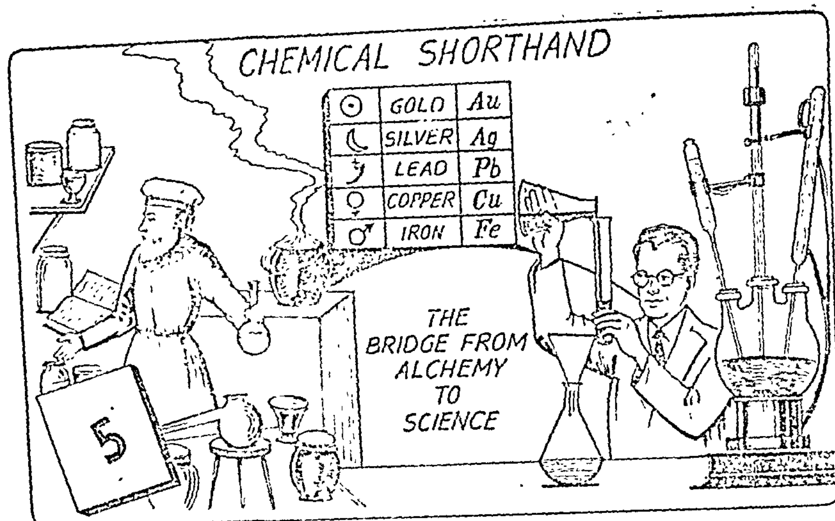
(*Delhi H.S. 1970, 68*)

3. Explain why sublimation is regarded as a physical change while slaking of lime a chemical change.

(*Punjab Pre-University 1962*)

4. Define the term chemical change. What conditions favour chemical changes ? Illustrate your answer with examples.

(*All-India H.S. 1967*)



Chemical Notation

1. **Chemical Shorthand.**—We always write U.S.A. as an abbreviation for the lengthy name, United States of America. In a similar way it is possible to devise a method for expressing the lengthy names of elements, composition of chemical compounds and the course of chemical reaction in a convenient and condensed form. This *system of chemical notation* merely conveys a large amount of information in a brief space and has nothing mysterious about it. Thus it is just a kind of *chemical shorthand.*



















Fig. 5·1—Some symbols used by alchemists.

2. **The Symbol.**—*The abbreviations used for the lengthy names of elements are termed symbols.*

The alchemists used symbols to represent elements and also compounds (*see* Fig. 5·1). These were not very intelligible, and different alchemists used different symbols. A number of these symbols were based upon astronomical objects while some others were mystical or had their origin in mythology.

Berzelius, a Swedish chemist, was the first to introduce the present system of using letters as symbols for elements. Now the first letter of the name of the element is used as its symbol. For example, Carbon, C; Nitrogen, N; Sulphur, S; Iodine I; Oxygen, O; Phosphorus, P.

There being 106 elements and only 26 letters in our alphabet, the names of several elements must begin with the same letter, *e.g.*, carbon, calcium, cadmium, cobalt, chromium and chlorine. In such cases the first letter along with another significant letter is used as the symbol. *The first letter of a symbol is always capital, but the second letter is always small.* Thus the symbols for the above elements are :

Carbon	C	Cobalt	Co
Chromium	Cr	Calcium	Ca
Copper	Cu	Chlorine	Cl
Cadmium	Cd		

(From *Cuprum*—Latin)



Jons Jacob Berzelius
(1779—1848)
A Swedish chemist who was responsible for the idea of representing elements by letters as symbols.

In case of elements known since long the names in various languages are radically different. Their symbols are derived from the Latin names. In the following table, in the case of elements where symbols have been derived from the Latin names, these are given in brackets.

Elements	Symbols	Approx At.wt.	Elements	Symbols	Approx. At. wt.
Aluminium	Al	27	Oxygen	O	16
Arsenic	As	75	Phosphorus	P	31
Barium	Ba	137	Sulphur	S	32
Bromine	Br	80	Zinc	Zn	65
Calcium	Ca	40	(From Latin names)		
Carbon	C	12	Antimony (*Stibium*)	Sb	122
Chlorine	Cl	35 5	Copper (*Cuprum*)	Cu	63·5
Chromium	Cr	52	Gold (*Aurum*)	Au	197
Cobalt	Co	59	Iron (*Ferrum*)	Fe	56
Fluorine	F	19	Lead (*Plumbum*)	Pb	207
Hydrogen	H	1	Mercury (*Hydrargyrum*)	Hg	200
Iodine	I	127	Potassium (*Kalium*)	K	39
Magnesium	Mg	24	Silver (*Argentum*)	Ag	108
Manganese	Mn	55	Sodium (*Natrium*)	Na	23
Nitrogen	N	14	Tin (*Stannum*)	Sn	119

A symbol for an element is more than a mere abbreviation. In addition to denoting particular element (*qualitative meaning*) it stands for a definite quantity of heat element (*quantitative meaning*).

For example, to a chemist, *the symbol C means one atom of carbon (the smallest and indivisible particle of carbon which can enter into combination with other elements) and also means 12 parts by weight of carbon (its atomic weight).*

3. The Formula, an Expression for the Molecule.—Since atoms of elements combine to form a complex form of matter called molecules, it seems logical to express the composition of a molecule in terms of appropriate symbols. *This symbolic expression for a molecule is called a* **formula.**

One atom of carbon combines with two atoms of oxygen to give a molecule of carbon dioxide. Formula of carbon dioxide can, therefore, be written as CO_2. It tells us the following :

(*i*) It represents *one* molecule of carbon dioxide. *Two* molecules of it will be written as $2CO_2$, and *three* as $3CO_2$.

(*ii*) It expresses that each molecule of carbon dioxide is made up of one atom of carbon and two atoms of oxygen.

(*iii*) It signifies 12 parts by weight of carbon and 32 parts by weight of oxygen (atomic weight=16).

(*iv*) It stands for 44 parts by weight of carbon dioxide which is the molecular weight of carbon dioxide.

4. Molecular Formulae of some Commoner Compounds.

Name	Formula	Name	Formula
Water ...	H_2O	Hydrochloric acid ...	HCl
Carbon monoxide ...	CO	Sulphuric acid ...	H_2SO_4
Carbon dioxide ...	CO_2	Nitric acid ...	HNO_3
Nitrous oxide ...	N_2O	Phosphoric acid ...	H_3PO_4
Nitric oxide ...	NO	Caustic soda or Sodium hydroxide ...	NaOH
Nitrogen trioxide ...	N_2O_3	Caustic potash or Potassium hydroxide ...	KOH
Nitrogen dioxide ...	NO_2	Silica ...	SiO_2
Nitrogen pentoxide ...	N_2O_5	Washing soda or Sodium carbonate ...	Na_2CO_3
Ammonia ...	NH_3		
Phosphine ...	PH_3		
Hydrogen sulphide ...	H_2S		

5. Percentage Composition of a Compound from its Formula.—The molecular weight of a compound can be obtained from the given formula, by adding together the atomic weights of all individual atoms in the molecule as represented by its formula. Let us use the formulae $CaCO_3$ and $KClO_3$ as examples :

$CaCO_3$			$KClO_3$		
Number of atoms	Atomic weight	Total weight	Number of atoms	Atomic weight	Total weight
1 of Ca	40	40	1 of K	39	39
1 of C	12	12	1 of Cl	35·5	35·5
3 of O	16	48	3 of O	86	48
Molecular weight=Total=100			Molecular weight=Total=122·5		

Percentage of any element in a compound can be calculated by dividing the total amount of that element by the molecular weight of the compound and multiplying the quotient by 100.

For example, weight of Ca, C and O in one molecule of $CaCO_3$ (mol. wt.=100) are 40, 12 and 48 respectively or percentage composition of $CaCO_3$ is : Ca=40% ; Ca=12% ; O=48%.

Similarly in the case of $KClO_3$ (mol. wt. 122·5), we have

$$\text{Percentage of } K=\frac{39}{122\cdot5}\times100=31\cdot84$$

$$\text{,, ,, } Cl=\frac{35\cdot5}{122\cdot5}\times100=28\cdot97.$$

$$\text{,, ,, } O=\frac{48}{122\cdot5}\times100=39\cdot18.$$

Example 1. *Calculate the percentage composition of (i) $KHSO_4$; and (ii) $ZnSO_4.7H_2O$ (K=39 ; Zn=65 ; S=32 ; O=16 ; H=1).*

(i) Mol. wt. of $KHSO_4$ $=39+1+32+64=136$

$$\text{Percentage of potassium} =\frac{\text{Wt. of potassium}}{\text{Mol. wt.}}\times100$$

$$=\frac{39}{136}\times100=28\cdot68.$$

$$\text{Similarly, percentage of hydrogen}=\frac{1}{136}\times100=0\cdot735$$

$$\text{,, ,, sulphur}=\frac{32}{136}\times100=23\cdot53$$

$$\text{,, ,, oxygen}=\frac{64}{136}\times100=47\cdot07.$$

(ii) Mol. wt. of $ZnSO_4.7H_2O=65+32+4\times16+7\times18$
$=65+32+64+126=287$

$$\text{Percentage of zinc}=\frac{65}{287}\times100=22\cdot65$$

$$\text{,, ,, sulphur}=\frac{32}{287}\times100=11\cdot15$$

$$\text{,, ,, oxygen}=\frac{64}{287}\times100=22\cdot30.$$

$$\text{Percentage of water of crystallization}=\frac{125}{287}\times100=43\cdot90$$

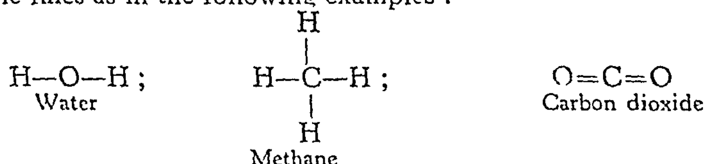
6. Empirical and Molecular Formulae.

The simplest formula which gives the simplest whole number ratio between the atoms of different elements present in the molecule of a substance is called its **Empirical or Simplest formula.**

The formula which gives the actual number of atoms of various elements present in the molecule of a substance is termed its **Molecular formula.**

For example, CH_2O is the empirical formula of glucose giving us the simplest ratio between atoms of various elements present as C : H : O :: 1 : 2 : 1. Molecular formula of glucose is $C_6H_{12}O_6$ giving us the actual number of various atoms present in the molecule. Similarly, empirical and molecular formulae for oxalic acid are CHO_2 and $C_2H_2O_4$ respectively.

7. **Structural Formula.**—*The structural formula of a compound is one showing how the various atoms in a compound are linked together.* The valency bonds are represented as single or double lines as in the following examples :



8. **Shapes of Molecules.**—Molecules which contain two atoms are necessarily linear but those containing three or more atoms may or may not be linear. For example, the molecule of CO_2 is linear whereas the two O—H bonds in H_2O are inclined at an angle of 104° 31′. Methane, CH_4 has a tetrahedral shape (*see* Fig. 5·2) with carbon at the centre of the tetrahedron and the four

Molecular formula	Structural formula	Ball-and-Stick Model	Space-filling Model
H_2 HYDROGEN	H—H		
CO_2 CARBON DIOXIDE	O=C=O		
H_2O WATER	H—O—H 104°		
NH_3 AMMONIA	H—N—H, H 108°		
CH_4	H, H—C—H, H 109°28′		

Fig. 5·2—Shapes of molecules.

hydrogen atoms at the four corners. The four C—H bonds are mutually inclined at an angle of 109° 28′. Ammonia, NH_3 has a pyramidal shape in which the observed angles between N—H, bonds are 108°.

9. **Calculation of Empirical Formula from Percentage Composition.**—We are given a box full of glass beads : 20% by weight being red each weighing 5 gm., 30% by weight being yellow each weighing 10 gm. and the remaining 50% by weight being blue each weighing 25 gm. *The relative number of red, yellow and blue beads can be easily found by dividing the percentage of each by its weight.*

Red = 20 ÷ 5 = 4 ; Yellow = 30 ÷ 10 = 3 ; Blue = 50 ÷ 25 = 2.

Thus we see that for every 4 red beads, there are 3 yellow ones and 2 blue ones.

In a similar manner, knowing the percentages of different elements in a molecule and their atomic weights, we can find the relative number of various atoms present therein. From these we can find the simplest whole number ratio between various atoms present and thus write the empirical formula of the compound

For solving numerical problems in which the simplest formula is to be calculated, we proceed as follows :

(i) Divide the percentage of each element by its atomic weight. This gives us *relative number of atoms.*

(ii) Find the ratio of quotients by dividing each one by the smallest quotient. This is *the simplest ratio.*

(iii) If the ratios are fractional, reduce them to the smallest possible whole numbers by multiplying throughout by a suitable integer. This gives the *simplest whole number ratio.*

(iv) Write down the symbols of various elements present side by side with the above numbers as subscripts to the lower right corner of each. This gives *the empirical or the simplest formula.*

Example 2. *What is the empirical formula of a substance having the following percentage composition : Oxygen=38·1% ; Hydrogen=0·8% ; Phosphorus=24·6% ; Sodium=36·5% (Na=23 ; P=31 ; O=16.)*

Proceeding as indicated above and writing the various steps in a tabular form, we have :

Element	Symbol	Percentage	At. Wt.	Relative No. of atoms	Simplest ratio
Sodium	Na	36·5	23	$\frac{36·5}{23}=1·59$	$\frac{1·59}{0·8}=2$
Hydrogen	H	0·8	1	$\frac{0·8}{1}=0·8$	$\frac{0·8}{0·8}=1$
Phosphorus	P	24·6	31	$\frac{24·6}{31}=0·8$	$\frac{0·8}{0·8}=1$
Oxygen	O	38·1	16	$\frac{38·1}{16}=2·38$	$\frac{2·38}{0·8}=3$

∴ *Empirical formula is* Na_2HPO_3.

Example 3. *A substance on analysis gave the following percentage composition : Na=29·11% ; S=40·50% ; O=30·38%. Calculate the empirical formula of the substance.*

Proceeding as usual and writing various steps in a tabular form, we have :

Element	Symbol	Percentage	At. wt.	Relative No. of atoms	Simplest ratio
Sodium	Na	29·11	23	$\frac{29·11}{23}=1·26$	$\frac{1·26}{1.26}=1$
Sulphur	S	40·50	32	$\frac{40·50}{32}=1·26$	$\frac{1·26}{1·26}=1$
Oxygen	O	30·38	16	$\frac{30·38}{}=1·89$	$\frac{1·89}{1·26}=1·5$

Simplest ratio as calculated above is fractional. Therefore, multiplying throughout by 2 to make it a whole number ratio, we have

The simplest whole number ratio as Na : S : O : : 2 : 2 : 3.

∴ *Empirical formula is* $Na_2S_2O_3$.

10. **Calculation of Molecular Formula.**—After calculating the empirical formula, the only way to find molecular formula is to find molecular weight which will be found to be some exact multiple of the empirical formula weight (say, x times), *i.e.*,

$$\frac{\text{Molecular weight}}{\text{Emp. formula weight}}=x.$$

The empirical formula (*taken x times*)=correct formula or the *molecular formula*.

Methods for determination of molecular weights are given in Chapter 13. For the present it will be worthwhile to just remember that

Molecular weight=2×Vapour density.

Example 4. *A compound contains 40% carbon, 6·66% hydrogen and the rest oxygen. Its vapour density is 30. Calculate its empirical and molecular formulae.*

(i) *Calculation of the Empirical formula :*

Proceeding as usual and writing various steps in the tabular form, we have :

Element	Symbol	Percentage	At. wt.	Relative No. of atoms	Simplest ratio
Carbon	C	40	12	$\frac{40}{12}=3·33$	$\frac{3·33}{3·33}=1$
Hydrogen	H	6·66	1	$\frac{6·66}{1}=6·66$	$\frac{6·66}{3·33}=2$
Oxygen *(By diff.)*	O	53·34	16	$\frac{53·34}{16}=3·33$	$\frac{3·33}{3·33}=1$

∴ *Empirical formula is* CH_2O.

(ii) *Calculation of Molecular formula :*

Empirical formula weight=12+2+16=30.

Molecular weight =2×Vapour density

=2×30 (*given*)=60

$$\frac{\text{Molecular weight}}{\text{Emp. formula wt.}}=\frac{60}{30}=2.$$

Molecular formula is Empirical formula (*taken 2 times*)

$=(CH_2O)_2=C_2H_4O_2$.

Example 5. *An organic liquid gave on analysis the following results : C=10·06% ; H=0·84% ; Cl=89·10%. A Victor Meyer determination gave its vapour density as 60. Find the molecular formula of the substance.*

(i) *Calculation of Empirical formula :*

Proceeding as usual and writing out various steps in a tabular form, we have :

Element	Symbol	Percentage	At wt	Relative No. of atoms	Simplest ratio
Carbon	C	10·06	12	$\frac{10·06}{12}=0·84$	$\frac{0·84}{0·84}=1$
Hydrogen	H	0·84	1	$\frac{0·84}{1}=0·84$	$\frac{0·84}{0·84}=1$
Chlorine	Cl	89·10	35·5	$\frac{89·10}{35·5}=2·5$	$\frac{2·5}{0·84}=3$

∴ *Empirical formula is* $CHCl_3$.

(ii) *Calculation of Molecular formula* :

Empirical formula weight $=12+1+3\times35{\cdot}5=119{\cdot}5$

Molecular weight $=2\times$ Vapour density $=2\times60=120$

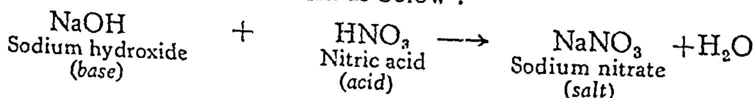
Now $\dfrac{\text{Molecular weight}}{\text{Empirical formula wt.}}=\dfrac{120}{119{\cdot}5}=1$

Hence the *Molecular formula is also* $CHCl_3$.

11. **Radical.**—The two parts constituting the molecule of any compound are separately called radicals, *e.g.*, silver and nitrate are the two radicals constituting the molecule of silver nitrate. A radical may be made up of one or more atoms of one or different kinds, *e.g.*, potassium (K), calcium (Ca), nitrate (NO_3), sulphate (SO_4). *Radicals are thus groups of atoms that react as single atoms, and keep their identity in many reactions.* It is a sort of synthetic element.

A radical is termed **Simple radical** when it is made up of one kind of atoms, *e.g.*, sodium (Na), barium (Ba), chloride (Cl), are all simple radicals. It is named **compound radical** when it is made up of two or more different kinds of atoms, *e.g.*, ammonium (NH_4) carbonate (CO_3) and sulphate (SO_4) are all compound radicals.

Sodium nitrate (*salt*) is obtained by neutralization of sodium hydroxide (*base*) with nitric acid as below :



$$\underset{\substack{\text{Sodium hydroxide}\\(\textit{base})}}{NaOH} + \underset{\substack{\text{Nitric acid}\\(\textit{acid})}}{HNO_3} \longrightarrow \underset{\substack{\text{Sodium nitrate}\\(\textit{salt})}}{NaNO_3} + H_2O$$

In the sodium nitrate molecule, sodium radical which was once a part of the base (*basic origin*) is called the **Basic radical**, while nitrate radical which has been derived from the acid is named the **Acid radical.**

Further the molecule of sodium nitrate on dissolving in water splits up (dissociates or ionizes) into sodium radical carrying a positive charge (Na^+—sodium ion) and a nitrate radical carrying a negative charge (NO_3^-—nitrate ion). Hence the sodium radical and the nitrate radical are also termed **Electropositive radical** and **Electronegative radical** respectively. Thus basic radicals are all electropositive radicals while acid radicals are all electronegative radicals.

12. **Valency as the Combining Capacity.**—Examine the formulae of the following compounds of hydrogen carefully :

HCl...Hydrogen chloride (Hydrochloric acid)

H_2O...Hydrogen oxide (Water)

H_3N...Hydrogen nitride (Ammonia)

H_4C...Hydrogen carbide (Methane).

We find that the number of Hydrogen atoms in each compound is different. *Chlorine has the capacity of holding one* hydrogen atom in a compound ; oxygen, two ; nitrogen, three ; and carbon, four. *This combining capacity of an element in terms of the number of hydrogen atoms that an atom can hold in a compound is called its* **Combining number** *or* **Valency.**

Thus valencies of chlorine, oxygen, nitrogen and carbon in the above compounds are 1, 2, 3, and 4 respectively. The combining capacity is also measured in terms of chlorine or oxygen atoms and it may be defined as *the number of chlorine atoms or double the number of oxygen atoms that an atom or a radical can hold in a compound.* Thus valency of phosphorus is 3 in PCl_3, that of sulphur is 6 in SO_3.*

13. **Elements with Variable Valency.**—Elements like iron, mercury, copper and tin are fickle enough to have more than one valency number. In these cases, the radical with lower valency is designated by *-ous*, while one with higher valency by *-ic*. For example :

$FeCl_2$ is ferrous chloride ;	$FeCl_3$ is ferric chloride.
Hg_2Cl_2 is mercurous ,, ;	$HgCl_2$ is mercuric ,,
$SnCl_2$ is stannous ,, ;	$SnCl_4$ is stannic ,,
CuCl is cuprous ,, ;	$CuCl_2$ is cupric ,,

14. **Common Radicals and their Valencies.**

Table I—Basic or Electropositive Radicals

Monovalent		Calcium	Ca	Trivalent	
Ammonium	NH_4	Cupric (*Copper*)	Cu	Aluminium	Al
Cuprous (*Copper*)	Cu	Ferrous	Fe		
Aurous (*Gold*)	Au	Magnesium	Mg	Auric (*Gold*)	Au
Hydrogen	H	Manganous	Mn	Chromic	Cr
Potassium	K	Mercuric	Hg	Ferric (*Iron*)	Fe
Silver	Ag	Mercurous	Hg_2		
Sodium	Na	Plumbous (*Lead*)	Pb	Tetravalent	
Bivalent		Stannous (*Tin*)	Sn	Stannic (*Tin*)	Sn
Barium	Ba	Strontium	Sr		
Cadmium	Cd	Zinc	Zn	Plumbic (*Lead*)	Pb

*For modern ideas on valency *see* Electronic Theory of Valency—THEORY OF CHEMICAL BONDING—*Chapter 10.*

Table II—Acid or Electronegative Radicals

Monovalent		Bisulphate	HSO_4	Stannate	SnO_3
		Acetate	CH_3COO	Zincate	ZnO_2
Fluoride	F	Permanganate	MnO_4		
Chloride	Cl	Cyanide	CN	**Trivalent**	
Bromide	Br				
Iodide	I	**Bivalent**		Borate	BO_3
Hypochlorite	ClO			Ferricyanide	$Fe(CN)_6$
Hypobromite	BrO	Oxide	O	Nitride	N
Hypoiodite	IO	Sulphide	S	Phosphide	P
Chlorate	ClO_3	Sulphite	SO_3	Phosphate	PO_4
Iodate	IO_3	Sulphate	SO_4	Arsenite	AsO_3
Hydride	H	Thiosulphate	S_2O_3	Arsenate	AsO_4
Hydroxide	OH	Carbonate	CO_3	Aluminate	AlO_3
Nitrite	NO_2	Chromate	CrO_4		
Nitrate	NO_3	Dichromate	Cr_2O_7	**Tetravalent**	
Meta-aluminate	AlO_2	Manganate	MnO_4		
Bicarbonate	HCO_3	Phosphite	HPO_3	Carbide	C
Bisulphite	HSO_3	Silicate	SiO_3	Ferrocyanide	$Fe(CN)_6$

15. **Writing of Formulae containing Radicals.**—The positive and the negative radicals combine in the inverse ratio of their valencies to give electrically neutral molecules. For writing a formula, containing radicals, we proceed as below :

(i) *Write down the symbols of the two radicals side by side with valencies at the top. Keep the positive radical to the left and the negative radical to the right.*

(ii) *Cross the valencies after dividing by the common factor, if any. Enclose a compound radical within bracket before putting any numeral to its lower right corner.*

The examples given below will make the rules clear :

Name of the Compound	*First step*	*Second step*
(1) Aluminium chloride	Al^3Cl^1	$AlCl_3$
(2) Ferric sulphate	$Fe^3SO_4{}^2$	$Fe_2(SO_4)_3$
[Enclosing the compound radical, SO_4 within brackets before crossing the valencies.]		
(3) Barium carbonate	$Ba^2CO_3{}^2$	$BaCO_3$
[Removing the common factor (=2) before crossing the valencies.]		
(4) Sodium bromide	Na^1Br^1	NaBr
(5) Chromium phosphate	$Cr^3PO_4{}^3$	$CrPO_4$
[Removing the common factor (=3) before crossing the valencies.]		
(6) Silver thiosulphate	$Ag^1S_2O_3{}^2$	$Ag_2S_2O_3$
(7) Ammonium dichromate	$NH_4{}^1Cr_2O_7{}^2$	$(NH_4)_2Cr_2O_7$
[Enclosing the compound radical, NH_4 within brackets before crossing the valencies.]		
(8) Calcium borate	$Ca^2BO_3{}^3$	$Ca_3(BO_3)_2$
[Enclosing the compound radical, BO_3 within brackets before crossing the valencies.]		

QUESTIONS AND PROBLEMS

Essay-type Questions

1. (a) Explain the terms symbol and formula. (*Punjab Pre-Uni. 1964*).

(b) What do you understand by the symbol 'C'? (*All India H.S. 1969*)

(c) What is the significance of the chemical formula CO_2? (*Punjab Pre-Univ. 1970*)

2. (a) What do you understand by the term 'valency' of an element? How is it measured? Mention the valency of each of the following elements:

Carbon, Nitrogen, Chlorine, Calcium and Mercury.

Give the formula of one compound of each in which the valency is fully justified.

(b) Find the valency of nitrogen in the following compounds:

N_2O, NO, N_2O_3, NO_2, N_2O_5. (*I.I.T. Adm. Test. 1969*)

3. (a) Explain the difference between Empirical formula, Chemical formula and Structural formula of a compound. (*Delhi H.S. 1964, Bihar 1966*)

(b) How will you write the formula of a compound knowing the valencies of its positive and negative radicals?

Formula Drill

4. Write formulae for the following:

(i) Zinc hydroxide (ii) Hydrogen sulphide
(iii) Stannous chloride (iv) Cupric chloride
(v) Zinc chloride (vi) Mercurous sulphate
(vii) Potassium sulphate (viii) Magnesium nitrate
(ix) Lead nitrate (x) Aluminium sulphate
(xi) Ferrous carbonate (xii) Manganous sulphite
(xiii) Silver oxide (xiv) Chromium sulphate
(xv) Potassium chlorate (xvi) Barium sulphite
(xvii) Calcium borate (xviii) Bismuth iodide
(xix) Ammonium chloride (xx) Sodium dichromate

5. The formula of radium bromide is $RaBr_2$. Write the formulae for the following compounds of radium.

(i) Radium permanganate, (ii) Radium phosphate, (iii) Radium sulphite. (*Punjab Pre-Univ. 1971*)

6. (a) Give chemical names for the following:

(i) $H_2S_2O_3$; (ii) $HMnO_4$; (iii) SiO_3^{-2}, (iv) $Fe(NO_3)_3$, (v) Calomel (*Delhi H.S. 1968*)

(b) Give the chemical formulae of the following compounds:

(i) Barium carbonate. (ii) Ferric phosphate (iii) Silver sulphide. (*Punjab Pre-Univ. 1970*)

Percentage Composition

7. (a) What information does a chemical formula convey?

(b) Find the percentage composition of the following compounds:

(i) Acetic acid, CH_3COOH, (ii) Copper sulphate, $CuSO_4.5H_2O$; (iii) Washing soda, $Na_2CO_3.10H_2O$. (*Chandigarh H.S 1970*)

Empirical Formula

8. A metal X having an atomic weight of 197 yields a chloride containing 35·1% of chlorine. Calculate the simplest formula (empirical formula) of the chloride. *(Senior Cambridge 1967 Nov.)*

9. 2·5 gm. of a metal on heating in air gave 2·95 gm. of the oxide. Calculate the empirical formula of the oxide. (At. wt. of the metal=238) *(Delhi H.S. 1967)*

10. Percentage of Europium (Eu) in one of its oxides is 86·4. What will be its empirical formula ? (At. wt. Eu=152) *(All India H.S. 1967)*

11. A crystalline salt on being rendered anhydrous loses 45·6% of its weight. The percentage composition of anhydrous salt is : Aluminium=10·5% ; Potassium=15·1% ; Sulphur=24·8% ; Oxygen=49·6%.

Find the simplest formula of the anhydrous and crystalline salt. *(Delhi H.S. 1964)*.

12. What is meant by empirical formula of a compound ? How is it related to its Molecular formula ?

Calculate the empirical formula of the substance having the following percentage composition :

O=38·1 ; H=0·8 ; P=24·6 ; Na=36·5.

Name the compound. *(Punjab Pre-University 1969)*.

Molecular Formula

13. On analysis a compound was found to contain H=9·09%, O=36·36% and C=54·54%. Its vapour density is 44. Calculate the molecular formula of the compound. *(Bihar H.S. 1964 Supp.)*.

14. Taking At. wt. of M=56 calculate the molecular formula of its oxide in which percentage of M=70. *(I.I.T. Admission Test 1963)*

15. An organic compound containing C, H and O has the following percentage composition :

C=32, H=4, O=difference.

Calculate its molecular formula if its molecule contains six oxygen atoms. *(I.I.T. Admission Test 1965)*

16. 3·164 gm. anhydrous zinc sulphate was placed in moist air at 25°C. After a few days its constant weight was 5·648 gm. Calculate the molecular formula of the hydrated salt at 25°C. *(I.I.T. Admission Test 1964)*

17. Percentage composition of an organic compound is as follows :

C=10·06, H=0·84 and Cl=89·10.

If its vapour density is 60, calculate its molecular formula. *(All India H.S. 1967)*

18. Percentage composition of a substance is as follows :

Na=29·11 ; S=40·5 and O=30·38.

Calculate its empirical formula. If its mol. wt.=158, find out its molecular formula. *(All India H.S. 1966)*

Test Your Understanding

19. Fill in the blanks in the following :

(i) A symbol stands for the......of a particular element and for a definite..... of that element.

(ii) The symbolic expression for a molecule is termed......

(iii) The simplest formula which gives the simplest whole number ratio between the atoms of different elements present in the molecule of the substance is termed......

(iv) Iron, copper and tin show ....valency.

(v) The .. of a compound is one showing how the various atoms in a compound are linked together.

KEY

(i) name, quantity ; (ii) formula ;

(iii) empirical formula ; (iv) variable ;

(v) structural formula.

ANSWERS

4. (i) $Zn(OH)_2$ (ii) H_2S (iii) $SnCl_2$
(iv) $CuCl_2$ (v) $ZnCl_2$ (vi) Hg_2SO_4
(vii) K_2SO_4 (viii) $Mg(NO_3)_2$ (ix) $Pb(NO_3)_2$
(x) Al_2S_3 (xi) $FeCO_3$ (xii) $MnSO_4$
(xiii) Ag_2O (xiv) $Cr_2(SO_4)_3$ (xv) $KClO_3$
(xvi) $BaSO_3$ (xvii) $Ca_3(BO_3)_2$ (xviii) BiI_3
(xix) NH_4Cl (xx) $Na_2Cr_2O_7$.

5. (i) $Ra(MnO_4)_2$; (ii) $Ra_3(PO_4)_2$; (iii) $RaSO_3$.

6. (a) (i) Thiosulphuric acid,
(ii) Permanganic acid,
(iii) Silicate ion, (iv) Ferric nitrate,
(v) Mercurous chloride, Hg_2Cl_2.
(b) (i) $BaCO_3$, (ii) $FePO_4$, (iii) Ag_2S.

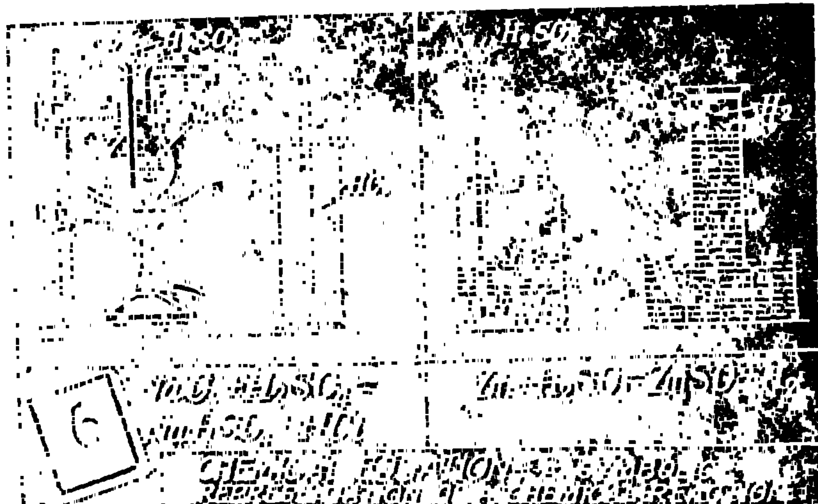
7. (i) C=40·00% ; H=6·67% ; O=53·33%.
(ii) Cu=25·45% ; S=12·82% ; O=25·64% ; H_2O=36·07%.
(iii) Na=16·08% ; C=4·19% ; O=16·78% ; H_2O=62·94%.

8. XCl_2. 9. M_2O_3. 10. [illegible]

11. $KAlS_2O_8$; $KAlS_2O_8.12H_2O$. 12. Na_2HPO_3 (Sodium Phosphite)

13. $C_4H_8O_2$. 14. M_2O_3. 15. $C_4H_4O_4$.

16. $ZnSO_4.7H_2O$. 17. $CHCl_3$. 18. $Na_2S_2O_3$.



Chemical Equations

1. What a Chemical Equation is ?—Chemical formula are used in representing molecules and their composition. Thes are helpful because they save time and aid our understanding They are doubly useful as they are often employed in equations t show how compounds have changed. *The shorthand method o expressing a chemical reaction with the help of formulae is calle a chemical equation.* Thus a chemical equation is an attempt t summarize, using chemical formulae, the essential features of reaction. It is a qualitative as well as a quantitative statement o the reactants and products in a chemical change.

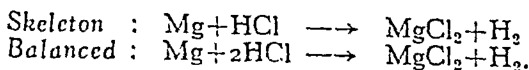
2. Steps in Writing Equations.—To write a chemica equation, proceed as follows :

(*a*) Write down the formulae of the reactants separatin them by plus signs to your left-hand side.

(*b*) Write down in the same way the formulae of the product and indicate by the use of an arrow (→) or an equal sign (=) tha a transformation has taken place. This gives us a skeleto equation.

(*c*) Balance the skeleton equation by equalising the numbe of various atoms on both sides. *Never change a formula to equa lise various atoms.* After balancing we get a balanced equation.

For example, writing an equation for the action of hydrochlo ric acid on magnesium to give magnesium chloride and hydroge we have



Skeleton : $Mg + HCl \longrightarrow MgCl_2 + H_2$

Balanced : $Mg + 2HCl \longrightarrow MgCl_2 + H_2$.

3. Essentials of a Chemical Equation.

(i) A chemical equation *represents an actual chemical change.* Before an equation can be written, the reactants and products of a chemical reaction must be known.

(ii) No atom is lost or gained during a chemical change, i.e., the law of Conservation of Mass (*see* Chapter 7) is obeyed. The number of atoms of a particular element should, therefore, be the same on both sides. In other words, *the equation should be balanced.*

(iii) A chemical reaction is only a rearrangement of atoms in the reacting molecules. *A chemical equation should, therefore, be molecular, i.e.,* the reactants as well as products should be represented as molecules.

4. Information conveyed by a Chemical Equation.—

A chemical equation expresses :

(*i*) The compounds taking part in the reaction.

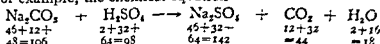
(*ii*) The compounds produced in the reaction.

(*iii*) The relative number of molecules of the reactants and the products.

(*iv*) The relative weights of the reactants and the products involved.

(*v*) The relative volumes of the reactants and the products in cases where gases are involved.

For example, the chemical equation



$$\underset{\substack{46+12+\\48=106}}{Na_2CO_3} + \underset{\substack{2+32+\\64=98}}{H_2SO_4} \longrightarrow \underset{\substack{46+32-\\64=142}}{Na_2SO_4} + \underset{\substack{12+32\\=44}}{CO_2} + \underset{\substack{2+16\\=18}}{H_2O}$$

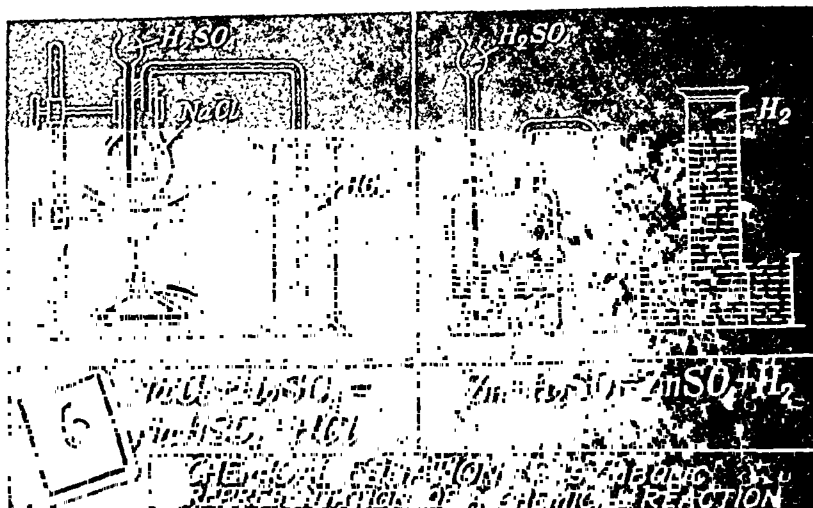
conveys us the following information :

(i) The sulphuric acid reacts with sodium carbonate under certain conditions, not clearly stated, to form sodium sulphate, carbon dioxide and water.

(ii) That 1 molecule of sodium carbonate (containing 2 atoms of sodium, 1 atom of carbon and 3 atoms of oxygen) reacts with 1 molecule of sulphuric acid (containing 2 atoms of hydrogen, 1 of sulphur and 4 of oxygen), to produce 1 molecule of sodium sulphate (containing 2 atoms of sodium, 1 of sulphur and 4 of oxygen), 1 molecule of carbon dioxide (containing 1 atom of carbon and 2 atoms of oxygen) and 1 molecule of water (containing 2 atoms of hydrogen and 1 of oxygen).

To the Student.—(*i*) Chemical equations involve formulae [illegible] the writing of correct formulae is essential for writing equations [illegible] equation containing an incorrect formula is not a true representation of a chemical change.

(ii) The knowledge of the chemical [illegible] the products—is essential before we write a chemical equation.



Chemical Equations

1. **What a Chemical Equation is ?**—Chemical formulae are used in representing molecules and their composition. These are helpful because they save time and aid our understanding. They are doubly useful as they are often employed in equations to show how compounds have changed. *The shorthand method of expressing a chemical reaction with the help of formulae is called a* **chemical equation.** Thus a chemical equation is an attempt to summarize, using chemical formulae, the essential features of a reaction. It is a qualitative as well as a quantitative statement of the reactants and products in a chemical change.

2. **Steps in Writing Equations.**—To write a chemical equation, proceed as follows :

(*a*) Write down the formulae of the reactants separating them by plus signs to your left-hand side.

(*b*) Write down in the same way the formulae of the products and indicate by the use of an arrow (→) or an equal sign (=) that a transformation has taken place. This gives us a **skeleton equation.**

(*c*) Balance the skeleton equation by equalising the number of various atoms on both sides. *Never change a formula to equalise various atoms.* After balancing we get a **balanced equation.**

For example, writing an equation for the action of hydrochloric acid on magnesium to give magnesium chloride and hydrogen, we have



Skeleton : $Mg + HCl \longrightarrow MgCl_2 + H_2$
Balanced : $Mg + 2HCl \longrightarrow MgCl_2 + H_2$.

3. Essentials of a Chemical Equation.

(*i*) A chemical equation *represents an actual chemical change.* Before an equation can be written, the reactants and products of a chemical reaction must be known.

(*ii*) No atom is lost or gained during a chemical change, *i.e.*, the law of Conservation of Mass (*see* Chapter 7) is obeyed. The number of atoms of a particular element should, therefore, be the same on both sides. In other words, *the equation should be balanced.*

(*iii*) A chemical reaction is only a rearrangement of atoms in the reacting molecules. *A chemical equation should, therefore, be molecular*, *i.e.*, the reactants as well as products should be represented as molecules.

4. Information conveyed by a Chemical Equation.—

A chemical equation expresses :

(*i*) The compounds taking part in the reaction.

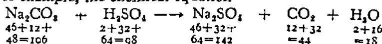
(*ii*) The compounds produced in the reaction.

(*iii*) The relative number of molecules of the reactants and the products.

(*iv*) The relative weights of the reactants and the products involved.

(*v*) The relative volumes of the reactants and the products in cases where gases are involved.

For example, the chemical equation



$$\underset{\substack{46+12+\\48=106}}{Na_2CO_3} + \underset{\substack{2+32+\\64=98}}{H_2SO_4} \longrightarrow \underset{\substack{46+32+\\64=142}}{Na_2SO_4} + \underset{\substack{12+32\\=44}}{CO_2} + \underset{\substack{2+16\\=18}}{H_2O}$$

conveys us the following information :

(*i*) The sulphuric acid reacts with sodium carbonate under certain conditions, not clearly stated, to form sodium sulphate, carbon dioxide and water.

(*ii*) That 1 molecule of sodium carbonate (containing 2 atoms of sodium, 1 atom of carbon and 3 atoms of oxygen) reacts with 1 molecule of sulphuric acid (containing 2 atoms of hydrogen, 1 of sulphur and 4 of oxygen), to produce 1 molecule of sodium sulphate (containing 2 atoms of sodium, 1 of sulphur and 4 of oxygen), 1 molecule of carbon dioxide (containing 1 atom of carbon and 2 atoms of oxygen) and 1 molecule of water (containing 2 atoms of hydrogen and 1 of oxygen).

To the Student.—(*i*) Chemical equations involve formulae and to master the writing of correct formulae is essential for writing equations. A chemical equation containing an incorrect formula is not a true representation of a chemical change.

(*ii*) The knowledge of the chemical reaction—the reactants and the products—is essential before we write a chemical equation.

(*iii*) That 106 gm. of sodium carbonate react with 98 gm. of sulphuric acid to produce 142 gm. of sodium sulphate, 44 gm. of carbon dioxide and 18 gm. of water.

(*iv*) That 22·4 litres of carbon dioxide at N.T.P. are liberated when 106 gm. of sodium carbonate react with 98 gm. of sulphuric acid.

5. **Limitations of Chemical Equation.**—Chemical equations are a useful mode of representing chemical changes and are understood by scientists all over the world. These cannot, however, represent all the facts. For example, they give us no information about the following :

(*i*) The physical state of the reactants whether solid or liquid, coarse or finely divided, etc.

(*ii*) Their concentration whether concentrated or dilute.

(*iii*) The time taken by the chemical reaction to complete.

(*iv*) Heat changes whether any heat is evolved or absorbed.

(*v*) The velocity of chemical reaction whether it is slow or fast.

(*vi*) Any other condition necessary for the chemical reaction, *e.g.*, pressure, temperature or any catalyst.

6. **Balancing of Equations.**—Two methods generally used for balancing chemical equations are : (*a*) The hit-and-trial method, and (*b*) the partial equations method.

7. **The Hit-and-trial Method.**—Simple chemical equations, wherein no one element is often repeated, are easily balanced by the hit-and-trial method. The systematic procedure for the same is :

(i) Select the atom which occurs at minimum number of places, first for balancing. Thus the atom which occurs at maximum number of places on both sides should be balanced last of all.

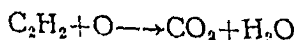
(ii) In reactions wherein an elementary gas like hydrogen, nitrogen or oxygen is either a reactant or a product, balance the equation keeping these gases in the atomic state. The equation so balanced is called **Atomic Equation.**

(iii) Multiply the atomic equation throughout by two to make it a **Molecular Equation.**

The following examples will illustrate the method :

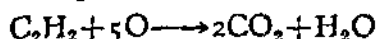
(1) *Burning of acetylene in oxygen to give carbon dioxide and water* is represented as follows :

(*a*) Writing *skeleton equation*, keeping oxygen in the atomic state, we get



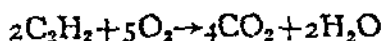
$$C_2H_2+O \longrightarrow CO_2+H_2O$$

(*b*) Balancing various atoms in the order C—H—O, we multiply, (*i*) CO_2 by 2 to equalise C-atoms, and (*ii*) O by 5 to equalise O-atoms. The *atomic equation*, so obtained, is



$$C_2H_2+5O\longrightarrow 2CO_2+H_2O$$

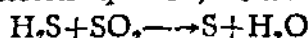
(*c*) Multiplying throughout by 2, we get the *molecular equation* :



$$2C_2H_2+5O_2\rightarrow 4CO_2+2H_2O$$

(2) *Oxidation of hydrogen sulphide by sulphur dioxide to give sulphur and water* is represented as follows :

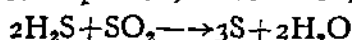
(*a*) Writing skeleton equation, we have



$$H_2S+SO_2\longrightarrow S+H_2O$$

(*b*) Balancing the various atoms in the order O—H—S, we multiply (*i*) H_2O by 2 to equalise oxygen atoms, and (*ii*) H_2S by 2 to equalise hydrogen atoms, and (*iii*) S by 3 to equalise sulphur atoms.

Thus the balanced equation, so obtained, is



$$2H_2S+SO_2\longrightarrow 3S+2H_2O$$

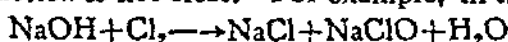
8. The Partial Equation Method.—The hit-*and*-trial method suffers from the following defects :

(*a*) Complicated equations wherein different elements are often repeated, take a very long time for balancing. As an example, *try to balance the following equation and see how long it takes to* balance :



$$Zn+HNO_3\longrightarrow Zn(NO_3)_2+N_2O+H_2O$$

(*b*) In some cases, balancing is of course easy but the *mechanism of the reaction* is not clear. For example, in the equation



$$NaOH+Cl_2\longrightarrow NaCl+NaClO+H_2O$$

balancing is very simple (multiply NaOH by 2 and it is balanced), but it is not clear how chlorine reacts with an alkali to give salts *of hydrochloric and hypochlorous acids.*

In all such cases, **Partial equations method** has been found very useful for balancing. This may be summarised as follows :

(*i*) The chemical reaction is supposed to proceed in two or more steps or stages.

(*ii*) Simple equations are written for these individual steps or stages and balanced by hit-and-trial method.

(*iii*) The *step equations* (called *partial equations*) are added in *such a way that* **Intermediate** *products* (*which do not appear in* the final products) cancel.

To the Student.—Never attempt to memorise balanced chemical equations. Learn more and more of chemical reactions—their reactants and product—write skeleton equations and balance yourself.

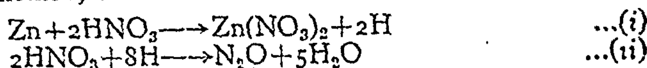
The following examples will explain the method :

Example 1. The chemical reaction between zinc and dilute nitric acid to give zinc nitrate, nitrous oxide and water is supposed to proceed in the following stages :

(*i*) Dilute nitric acid first reacts with zinc to give zinc nitrate and nascent hydrogen (*Intermediate product*).

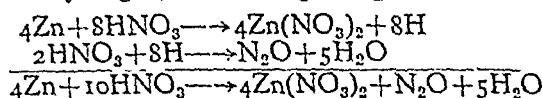
(*ii*) Nascent hydrogen next reduces nitric acid to nitrous oxide and water.

Writing partial equations for the two stages and balancing by hit-and-trial method, we have



$$Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + 2H \quad ...(i)$$
$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O \quad ...(ii)$$

Multiplying equation (*i*) by 4, cancelling the intermediate product (nascent hydrogen) and adding, we get



$$4Zn + 8HNO_3 \longrightarrow 4Zn(NO_3)_2 + 8H$$
$$2HNO_3 + 8H \longrightarrow N_2O + 5H_2O$$
$$\overline{4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O}$$

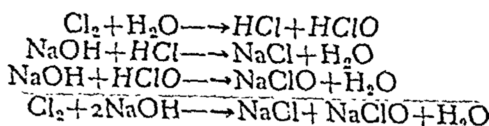
Example 2. The chemical reaction between chlorine and sodium hydroxide to give sodium chloride, sodium, hypochlorite and water is supposed to proceed in the following stages :

(*i*) Chlorine first reacts with water to give hydrochloric acid and hypochlorous acid (*Intermediate product*).

(*ii*) Hydrochloric acid then reacts with sodium hydroxide to give sodium chloride and water.

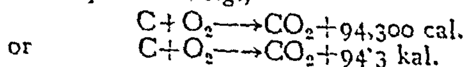
(*iii*) Hypochlorous acid reacts with sodium hydroxide to produce sodium hypochlorite and water.

Writing partial equations for these stages and adding these step equations in such a way that the intermediate products (written in italics) cancel, we have



$$Cl_2 + H_2O \longrightarrow \mathit{HCl} + \mathit{HClO}$$
$$NaOH + \mathit{HCl} \longrightarrow NaCl + H_2O$$
$$NaOH + \mathit{HClO} \longrightarrow NaClO + H_2O$$
$$\overline{Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O}$$

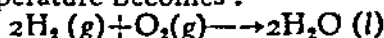
9. Thermochemical Equations.—Chemical equations for exothermic or endothermic reactions representing the quantity of heat evolved or absorbed during the reaction, are called **thermochemical equations**, *e.g.*,



$$C + O_2 \longrightarrow CO_2 + 94{,}300 \text{ cal.}$$
or
$$C + O_2 \longrightarrow CO_2 + 94{\cdot}3 \text{ kal.}$$

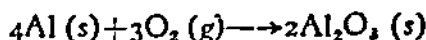
From the equation we learn that when 12 gm. of carbon combine with 32 gm. of oxygen on burning to give carbon dioxide, 94,300 calories or 94·3 kcal. (kilogram-calories) of heat are evolved.

10. Physical States of Reactants and Products.—It is quite helpful if an equation gives an idea about the physical state of reactants and products of a chemical reaction. This is indicated by writing letters (*g*), (*l*), or (*s*) to represent gas, liquid or solid respectively. Thus the equation for the production of water by the reaction of hydrogen and oxygen (in the presence of an electric spark) at room temperature becomes :



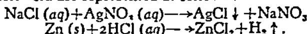
$$2H_2\,(g)+O_2(g)\longrightarrow 2H_2O\,(l)$$

Burning of aluminium in oxygen to form aluminium oxide can be written as :

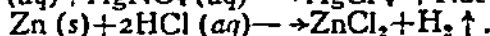


$$4Al\,(s)+3O_2\,(g)\longrightarrow 2Al_2O_3\,(s)$$

In case a product is precipitated, it is indicated by an arrow pointing downwards (↓) while a gaseous product is indicated by an arrow pointing upwards (↑). A reactant in aqueous solution is indicated by putting (*aq*) after its symbol. For precipitation of silver chloride on mixing aqueous solutions of sodium chloride and silver nitrate and evolution of hydrogen when zinc reacts with hydrochloric acid are represented as follows :



$$NaCl\,(aq)+AgNO_3\,(aq)\longrightarrow AgCl\downarrow+NaNO_3$$



$$Zn\,(s)+2HCl\,(aq)\longrightarrow ZnCl_2+H_2\uparrow.$$

QUESTIONS

Essay-type Questions :

1. Using as an example, the equation



$$2Na+2H_2O\longrightarrow 2NaOH+H_2$$

explain (*a*) How an equation is obtained ?

(*b*) What information is conveyed by an equation ?

(*c*) What important facts are not shown by an equation ?

(*Delhi H.S. 1966, 63 ; Punjab H S. 1963 ; All India H S. 1968 ; Punjab Pre-Univ. 1963 , Punjab Inter. 1960*)

2. What is a chemical equation and on what principles is it formed ? Show clearly giving suitable examples the information conveyed by an equation. What are its defects ? (*U.P. Board Inter. 1961 ; Delhi H.S. 1966*)

4. How are the following informations symbolised in a chemical equation :

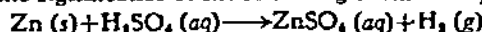
(*i*) A precipitate being formed,

(*ii*) A reactant being in an aqueous solution,

(*iii*) A gaseous product being evolved, and

(*iv*) A reaction being exothermic. (*Delhi H.S. 1970*)

5. Give the significance of the following chemical equation :



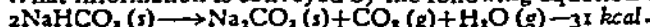
$$Zn\,(s)+H_2SO_4\,(aq)\longrightarrow ZnSO_4\,(aq)+H_2\,(g)$$

[Atomic weights—Zn=65 ; H=1 , S=32 ; O=16].

(*Punjab Pre-Univ. 1971*)

6. State the principle on which balancing of chemical equations is primarily based. (*Punjab Pre-Univ. 1970*)

7. What information is conveyed by the following equation ?



$$2NaHCO_3\,(s)\longrightarrow Na_2CO_3\,(s)+CO_2\,(g)+H_2O\,(g)-31\,kcal.$$

Equation Drill

8. Translate the following equations written in words into language of chemistry.

(1) Calcium oxide+Water=Calcium hydroxide.

(2) Barium chloride+Sodium sulphate=Barium sulphate+Sodium chloride.

(3) Zinc+Sulphur=Zinc sulphide.

(4) Ammonium chloride+Sodium nitrite=Sodium chloride+Water +Nitrogen.

(5) Aluminium+Water (steam)=Aluminium oxide+Hydrogen.

(6) Calcium bicarbonate+Calcium oxide=Calcium carbonate +Water.

(7) Zinc+Sulphuric acid (dil.)=Zinc sulphate+Hydrogen.

(8) Zinc+Sulphuric acid (conc.)=Zinc sulphate+Sulphur dioxide+ Water.

(9) Sodium carbonate+Hydrochloric acid=Sodium chloride+ Carbon dioxide+Water.

(10) Sodium hydroxide+Hydrochloric acid=Sodium chloride+ Water.

9. Balance the following equations by *hit-and-trial* method :

(*a*) (*i*) $Zn+HCl \rightarrow ZnCl_2+H_2$

(*ii*) $Cu+H_2SO_4 \rightarrow CuSO_4+SO_2+H_2O$

(*iii*) $NH_4Cl+Ca(OH)_2 \rightarrow CaCl_2+NH_3+H_2O$

(*iv*) $NH_4Cl+NaNO_2 \rightarrow NaCl+N_2+H_2O$

(*b*) (*i*) $KMnO_4+H_2SO_4 \rightarrow K_2SO_4+MnSO_4+H_2O+O_2$

(*ii*) $As_4O_6+SnCl_2+HCl \rightarrow SnCl_4+As+H_2O$

(*iii*) $C_2H_2+O_2 \rightarrow CO_2+H_2O$

(*iv*) $Cu+HNO_3 \rightarrow Cu(NO_3)_2+NO+H_2O$

10. Translate the following equations written in words into language chemistry :

(1) Sodium chloride+Sulphuric acid=Sodium bisulphate+Hydro· chloric ac

(2) Ammonium nitrite=Nitrogen+Water.

(3) Sodium chloride+Silver nitrate=Silver chloride+Sodium nitra

(4) Magnesium+Nitrogen=Magnesium nitride.

(5) Calcium carbonate+Hydrochloric acid=Calcium chloride+ Carbon dioxide+Wat

(6) Potassium nitrate+Sulphuric acid=Potassium bisulphate+ Nitric aci

(7) Sodium sulphide+Hydrochloric acid=Sodium chloride+Sulph dioxide+Wat

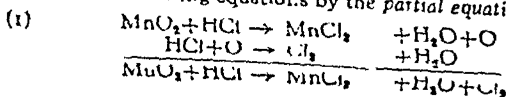
(8) Calcium hydroxide+Carbon dioxide=Calcium carbonate+ Wat

(9) Sulphur+Sulphuric acid=Sulphur dioxide+Water.

(10) Carbon+Sulphuric acid=Carbon dioxide+Sulphur dioxide+ Wate

11. Balance the following equations by the *partial equations method* :—

(1)



(2)
$$NaCl+H_2SO_4 \rightarrow NaHSO_4 + HCl$$
$$MnO_2+H_2SO_4 \rightarrow MnSO_4 + H_2O+O$$
$$HCl+O \rightarrow Cl_2 + H_2O$$
$$\overline{NaCl+MnO_2+H_2SO_4 \rightarrow NaHSO_4 + MnSO_4+H_2O+Cl_2}$$

(3)
$$Cl_2+H_2O \rightarrow HCl + O$$
$$FeSO_4+H_2SO_4+O \rightarrow Fe_2(SO_4)_3 + H_2O$$
$$\overline{FeSO_4+H_2SO_4+Cl_2 \rightarrow Fe_2(SO_4)_3 + HCl}$$

(4)
$$Cl_2+H_2O \rightarrow HCl + O$$
$$H_2S+O \rightarrow S + H_2O$$
$$\overline{H_2S+Cl_2 \rightarrow HCl + S+H_2O}$$

(5)
$$KMnO_4+H_2SO_4 \rightarrow K_2SO_4 + MnSO_4+H_2O+O$$
$$H_2S+O \rightarrow S + H_2O$$
$$\overline{KMnO_4+H_2SO_4+H_2S \rightarrow K_2SO_4 + MnSO_4+H_2O+S}$$

(6)
$$K_2Cr_2O_7+H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3+H_2O+O$$
$$SO_2+O+H_2O \rightarrow H_2SO_4$$
$$\overline{K_2Cr_2O_7+H_2SO_4+SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3+H_2O}$$

(7)
$$HNO_3 \rightarrow NO_2 + H_2O+O$$
$$H_2S+O \rightarrow S + H_2O$$
$$\overline{HNO_3+H_2S \rightarrow NO_2 + H_2O+S}$$

(8)
$$SO_2+H_2O \rightarrow H_2SO_4 + H$$
$$Fe_2(SO_4)_3+H \rightarrow FeSO_4 + H_2SO_4$$
$$\overline{Fe_2(SO_4)_3+SO_2+H_2O \rightarrow FeSO_4 + H_2SO_4}$$

(9)
$$Cu+H_2SO_4 \rightarrow CuO + SO_2+H_2O$$
$$CuO+H_2SO_4 \rightarrow CuSO_4 + H_2O$$
$$\overline{Cu+H_2SO_4 \rightarrow CuSO_4 + SO_2+H_2O}$$

(10)
$$Zn+HNO_3 \rightarrow Zn(NO_3)_2 + H$$
$$HNO_3+H \rightarrow N_2O + H_2O$$
$$\overline{Zn+HNO_3 \rightarrow Zn(NO_3)_2 + N_2O+H_2O}$$

Test Your Understanding :

12. Fill in the blanks in the following :

(i) Shorthand method of writing a chemical reaction with the help of......is called......

(ii) A chemical equation should be......and ....

(iii) $C+O_2 \rightarrow CO_2+94.3$ kcal. is an example of a.........representing an......(endothermic/exothermic) reaction.

KEY

(i) formulae, an equation ; (ii) balanced, molecular ; (iii) Thermochemical equation, exothermic.

ANSWERS

8. (1) $CaO+H_2O=Ca(OH)_2$

(2) $BaCl_2+Na_2SO_4=BaSO_4+2NaCl$

(3) $Zn+S=ZnS$

(4) $NH_4Cl+NaNO_2=NaCl+2H_2O+N_2$

(5) $2Al+3H_2O=Al_2O_3+3H_2$

(6) $Ca(HCO_3)_2+CaO=2CaCO_3+H_2O$

(7) $Zn+H_2SO_4=ZnSO_4+H_2$

(8) $Zn+2H_2SO_4=ZnSO_4+SO_2+2H_2O$

(9) $Na_2CO_3+2HCl=2NaCl+CO_2+H_2O$

(10) $NaOH+HCl=NaCl+H_2O$

9. (a) (i) $Zn+2HCl=ZnCl_2+H_2$

(ii) $Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$

(iii) $2NH_4Cl+Ca(OH)_2=CaCl_2+2NH_3+2H_2O$

(iv) $NH_4Cl+NaNO_2=NaCl+N_2+2H_2O$

(b) (i) $$4KMnO_4+6H_2SO_4 \rightarrow 2K_2SO_4+4MnSO_4+6H_2O+5O_2$$

(ii) $$As_4O_6+6SnCl_2+12HCl \rightarrow 6SnCl_4+4As+6H_2O$$

(iii) $$2C_2H_2+5O_2 \rightarrow 4CO_2+2H_2O$$

(iv) $$3Cu+8HNO_3 \rightarrow 3Cu(NO_3)_2+2NO+4H_2O$$

10. (1) $$NaCl+H_2SO_4=NaHSO_4+HCl$$

(2) $$NH_4NO_2=N_2+2H_2O$$

(3) $$NaCl+AgNO_3=AgCl+NaNO_3$$

(4) $$3Mg+N_2=Mg_3N_2$$

(5) $$CaCO_3+2HCl=CaCl_2+CO_2+H_2O$$

(6) $$KNO_3+H_2SO_4=KHSO_4+HNO_3$$

(7) $$Na_2SO_3+2HCl=2NaCl+SO_2+H_2O$$

(8) $$Ca(OH)_2+CO_2=CaCO_3+H_2O$$

(9) $$S+2H_2SO_4=3SO_2+2H_2O$$

(10) $$C+2H_2SO_4=CO_2+2SO_2+2H_2O$$

11. (1)
$$MnO_2+2HCl \rightarrow MnCl_2+H_2O+O$$
$$2HCl+O \rightarrow Cl_2+H_2O$$
$$\overline{MnO_2+4HCl \rightarrow MnCl_2+Cl_2+2H_2O}$$

(2)
$$NaCl+H_2SO_4 \rightarrow NaHSO_4+HCl] \times 2$$
$$MnO_2+H_2SO_4 \rightarrow MnSO_4+H_2O+O$$
$$2HCl+O \rightarrow Cl_2+H_2O$$
$$\overline{2NaCl+MnO_2+3H_2SO_4 \rightarrow 2NaHSO_4+MnSO_4+Cl_2+2H_2O}$$

(3)
$$Cl_2+H_2O \rightarrow 2HCl+O$$
$$2FeSO_4+H_2SO_4+O \rightarrow Fe_2(SO_4)_3+H_2O$$
$$\overline{2FeSO_4+H_2SO_4+Cl_2 \rightarrow Fe_2(SO_4)_3+2HCl}$$

(4)
$$Cl_2+H_2O \rightarrow 2HCl+O$$
$$H_2S+O \rightarrow S+H_2O$$
$$\overline{H_2S+Cl_2 \rightarrow 2HCl+S}$$

(5)
$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5O$$
$$H_2S+O \rightarrow S+H_2O] \times 5$$
$$\overline{2KMnO_4+3H_2SO_4+5H_2S \rightarrow K_2SO_4+2MnSO_4+5S+8H_2O}$$

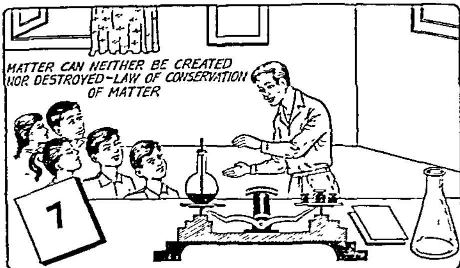
(6)
$$K_2Cr_2O_7+4H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O$$
$$SO_2+O+H_2O \rightarrow H_2SO_4] \times 3$$
$$\overline{K_2Cr_2O_7+H_2SO_4+3SO_2 \rightarrow K_2SO_4+Cr_2(SO_4)_3+H_2O}$$

(7)
$$2HNO_3 \rightarrow 2NO+H_2O+3O$$
$$H_2S+O \rightarrow S+H_2O] \times 3$$
$$\overline{2HNO_3+3H_2S \rightarrow 2NO+4H_2O+3S}$$

(8)
$$SO_2+2H_2O \rightarrow H_2SO_4+2H$$
$$Fe_2(SO_4)_3+2H \rightarrow 2FeSO_4+H_2SO_4$$
$$\overline{Fe_2(SO_4)_3+SO_2+2H_2O \rightarrow 2FeSO_4+2H_2SO_4}$$

(9)
$$Cu+H_2SO_4 \rightarrow CuO+SO_2+H_2O$$
$$CuO+H_2SO_4 \rightarrow CuSO_4+H_2O$$
$$\overline{Cu+2H_2SO_4 \rightarrow CuSO_4+SO_2+2H_2O}$$

(10)
$$Zn+2HNO_3 \rightarrow Zn(NO_3)_2+2H] \times 4$$
$$2HNO_3+8H \rightarrow N_2O+5H_2O$$
$$\overline{4Zn+10HNO_3 \rightarrow 4Zn(NO_3)_2+N_2O+5H_2O.}$$



Laws of Chemical Combination

1. Laws of Stoichiometry.—As a result of quantitative experiments on chemical changes five general laws were discovered. These are called *laws of stoichiometry* or the *laws of chemical combination*. They are:

(i) The *Law of Conservation of Mass* or the *Law of Indestructibility of Matter.*

(ii) The *Law of Consant Proportions* or the *Law of Definite Proportions.*

(iii) The *Law of Multiple Proportions.*

(iv) The *Law of Reciprocal Proportions* or the *Law of Equivalent Proportions.*

(v) The *Law of Gaseous Volumes.*

2. The Law of Conservation of Mass (*Lavoisier, 1744*).—The law states:

Matter is neither created, nor destroyed as a result of any chemical change. This is also called the *Law of Indestructibility of Matter.* The truth of the law can be easily demonstrated in the laboratory as follows:

Expt. 1. Take a small piece of dry phosphorus in a strong round-bottom flask dried beforehand and weigh it. Heat gently the spot where phosphorus lies till it catches fire. When the phosphorus burns away and disappears, cool the flask and re-weight. The weight will be found to have remained unchanged.

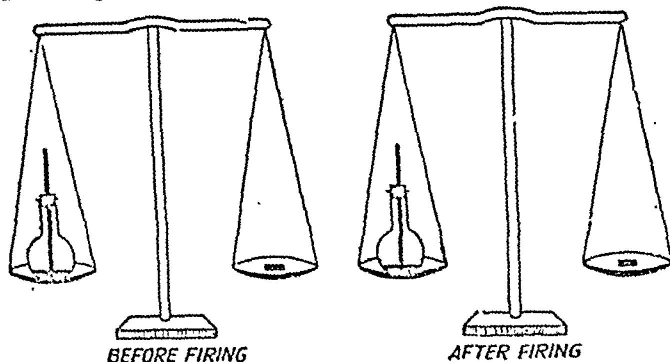


Fig. 7'1—In a chemical reaction (burning of phosphorus) mass of reactants=mass of products.

H. Landolt (1893—1908) studied a series of chemical reac tions not accompanied by production or absorption of mucl heat, *e.g.*,



(i) $Ag_2SO_4 + 2FeSO_4 \rightarrow 2Ag + Fe_2(SO_4)_3$



(ii) $5HI + \underset{\text{Iodic acid}}{HIO_3} \rightarrow 3I_2 + 3H_2O$

He sealed the two solutions to be reacted in the two limbs of a Jena glass H-tube (Fig. 7'2), weighed the sealed tube accurately, made the two solutions react and weighed again after cooling to the original temperature. He found that in all these experiments the weight remained unchanged showing the truth of the law.

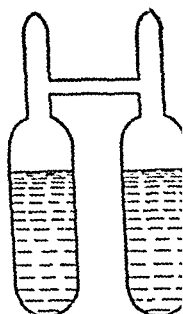


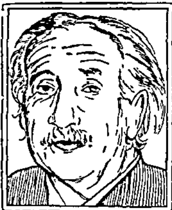
Fig. 7'2—
Landolt's tub

According to Einstein's Theory of Relativity mass and energy are interconvertible: $E = mc^2$, where E is the energy liberated with the disappearance of mass m and c is the velocity of light. According to this a chemical change involving a production of energy ($=E$) will be accompanied by a loss of mass, $m = E/c^2$.

But as c is very large, m is quite negligible in ordinary rea tions. Hence the law is quite valid for ordinary quantitative wo in the laboratory and should rather be stated as: *There is detectable change in mass in an ordinary chemical reaction.* will be interesting to note that 3¾ tons of phosphorus have to burnt to cause a loss in weight=1 mgm.

3. **The Law of Constant Proportions.**—The law of c stant or definite proportions as stated by Proust in 1797 states

a chemical compound is always found to be made up of the same elements combined together in the same proportion by weight.



Albert Einstein
(1879—1955)
Austrian-Swiss-American physicist, he was the author of the Theory of Relativity. He received the Nobel Prize for Physics in 1921.



Louis Proust
(1755—1826)
A French chemist, he was one of the first to observe that elements always combine with one another in a *definite ratio* by weight.

For example, pure water, from whatever source (well, river, etc.) or country (India, Pakistan or America) it may be taken, will always be found to be made up of only hydrogen and oxygen (*same elements*) combined together in the *fixed ratio* of 1 : 8 by weight. This ratio has been fixed by nature and cannot be changed.

A sample of cupric oxide may be prepared in the laboratory by heating copper carbonate, copper nitrate or copper powder. In each case, it will be found to be made up of the *same elements* (copper and oxygen) combined together in the *fixed ratio*, 4 : 1 by weight.

Example 1. *1·375 gm. of cupric oxide were reduced by heating in a current of hydrogen and the weight of copper that remained was 1·098 gm. In another experiment [illegible] gm. of copper were dissolved in nitric acid and the resulting copper nitrate converted to cupric oxide by ignition. The weight of cupric oxide formed was 1·476 gm. Show that these results illustrate the Law of Constant Proportions.* (*Delhi H.S. 1952*)

In the first experiment :

Weight of cupric oxide taken $= 1·375$ gm.

Wt. of copper obtained on reduction $= 1·098$ gm.

% of copper in cupric oxide $= \frac{1·098 \times 100}{1·375} =$ [illegible]

% of oxygen „ „ $= 100 - 79·85 =$ [illegible]

In the second experiment :

Weight of copper taken $=1·179$ gm.

Wt. of cupric oxide obtained $=1·476$ gm.

% of copper in cupric oxide $=\frac{1·179 \times 100}{1·476}=79·89$

% of oxygen ,, ,, ,, $=100-79·89=20·11$

Percentage composition of cupric oxide in the two experiments is found to be practically the same. This illustrates the law of constant proportions.

4. **Law of Multiple Proportions.**—The Law of Multiple Proportions, as stated by Dalton in 1803, states : *If two elements A and B combine to give two or more compounds, then weights of A which combine with a fixed weight of B, bear a simple ratio to one another.*

For example, carbon and oxygen combine to give two compounds, *viz.*, carbon monoxide and carbon dioxide. The weights of oxygen which combine with a fixed weight of carbon (=12, say) in these oxides are 16 and 32 respectively. These bear the simple ratio, 1 : 2, to each other.

Similarly, sulphur and oxygen combine to give two compounds, *viz.*, sulphur dioxide (SO_2) and sulphur trioxide (SO_3). Weights of oxygen which combine with a fixed weight of sulphur (=32, say) are 32 and 48 respectively. These bear the simple ratio, 2 : 3, to each other.

The truth of the law can be verified experimentally in the laboratory as follows :

Expt. 2. Take 1 gm. each of black and red oxides of copper and reduce by heating in a current of hydrogen. Weigh the metallic copper obtained. From the weight of the metallic copper obtained in each case calculate the weights of oxygen that combine with a definite weight of copper in the two cases. These weights of oxygen will bear a simple ratio to one another.

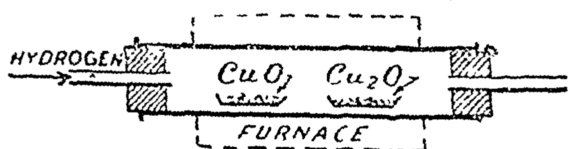


Fig. 7·3—Reduction of copper oxide by heating in a current of hydrogen.

Example 2. *The oxides of lead were separately reduced to metallic lead by heating in a current of hydrogen and the following data obtained :*

(a) *Weight of yellow oxide taken* $=3·45$ *gm.*
Loss in weight during reduction $=0·24$ *gm.*

(b) *Weight of brown oxide taken* $=1·195$ *gm.*
Loss in weight during reduction $=0·16$ *gm.*

Show that the above data illustrates the law of multiple proportions.

Loss in weight during reduction in the above cases is due to loss of oxygen.

Weight of yellow oxide taken	=3·45 gm.
,, ,, oxygen lost	=0·24 gm.
,, ,, lead obtained	=3·45−0·24=3·21 gm.
Weight of brown oxide taken	=1·195 gm.
,, ,, oxygen lost	=0·16 gm.
,, ,, lead obtained	=1·195−0·16
	=1·035 gm.

1·035 gm. of lead combines with 0·16 gm. of oxygen in brown oxide.

Wt. of lead which will combine with 0·24 gm. of oxygen

$$= \frac{1·035}{0·16} \times 0·24$$

$$= 1·0552 \text{ gm.}$$

Weights of lead which combine with a fixed weight of oxygen (=0·24 gm.) are 3·21 gm. and 1·552 gm. respectively in the two oxides. These bear a simple ratio 2 : 1 to each other within experimental error and thus illustrate the law of multiple proportions.

Example 3. *On analysis it was found that the black oxide of copper, the red oxide of copper, litharge, the red oxide of lead and the dioxide of lead contain 79·9%, 88 8%, 92·8%, 90·6% and 86·6% respectively of metal. Establish the law of multiple proportions with the help of this data.*

% of copper in black oxide	=79·9
,, ,, oxygen ,, ,,	=100−79·9=20·1

Weight of copper which combines with 1 gm. of oxygen in black oxide $= \frac{79·9}{20·1} = 3·975$ gm.

% of copper in red oxide	=88·8
,, ,, oxygen ,, ,,	=100−88·8=11·2

Weight of copper which combines with 1 gm. of oxygen in red oxide $= \frac{88·8}{11·2} = 7·929$ gm.

Weights of copper which combine with a fixed weight of oxygen (=1 gm.) are 3·975 gm. and 7·929 gm. respectively in the two oxides. These bear the simple ratio 1 : 2 to each other and thus illustrate the law of multiple proportions.

% of lead in litharge	=92·8
,, ,, oxygen ,, ,,	=100−92·8=7·2

Wt. of lead which combines with 1 gm. of oxygen in litharge $= \frac{92·8}{7·2} = 12·98$ gm.

% of lead in red lead $= 90{\cdot}6$

,, ,, oxygen ,, ,, $= 100 - 90{\cdot}6 = 9{\cdot}4$

Wt. of lead which combines with 1 gm. of oxygen in red lead $= \frac{90{\cdot}6}{9{\cdot}4} = 9{\cdot}638$ gm.

% of lead in lead oxide $= 86{\cdot}6$

,, ,, oxygen ,, ,, $= 100 - 86{\cdot}6 = 13{\cdot}4$

Wt. of lead which combines with 1 gm. of oxygen in lead dioxide $= \frac{86{\cdot}6}{13{\cdot}4} = 6{\cdot}463$ gm.

Weights of lead which combine with a fixed weight of oxygen (1 gm.) are 12·89 gm., 9·638 gm. and 6·463 gm. respectively in the three oxides. These bear the simple ratio 4 : 3 : 2 to one another and thus illustrate the law of multiple proportions.

5. **The Law of Reciprocal Proportions.**—The law of Reciprocal or Equivalent Proportions as stated by Richter in 1792 is as under :

Weights of two elements A and B, which separately combine with a fixed weight of a third element C, are either the same or simple multiples of the weights of A and B which combine with each other.

For example, both sulphur and oxygen separately combine with hydrogen to give hydrogen sulphide (H_2S) and water (H_2O) respectively. Weights of sulphur and oxygen which separately combine with a fixed weight of hydrogen (=1, say) are 16 and 8 respectively. Now whenever sulphur and oxygen combine, they will always do so in the ratio 16 : 8, or a simple multiple thereof.

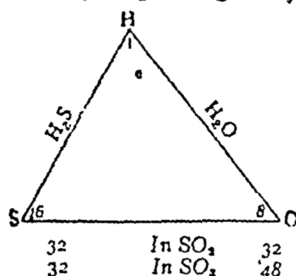


Fig. 7·4

In sulphur dioxide (SO_2), sulphur and oxygen combine in the ratio 32 : 32—a multiple of the ratio 16 : 8. The two ratios 16 : 8 and 32 : 32 are simply related to each other as 2 : 1 $\left[\because \frac{16}{8} : \frac{32}{32} :: 2 : 1 \right]$.

In sulphur trioxide (SO_3), the two elements combine in the ratio 32 : 48—simply related to the ratio 16 : 8 as 1 : 3.

Similarly 14 parts by weight of nitrogen or 24 parts by weight of oxygen separately combine with a fixed weight (=3) of hydrogen in ammonia (NH_3) and water (H_2O) respectively.

According to the law of reciprocal proportions 14 parts by weight of nitrogen are equivalent to 24 parts by weight of oxygen and when nitrogen and oxygen combine they will do so in the ratio 14 : 24 by weight or a simple multiple thereof. In nitrogen trioxide (N_2O_3) these are actually present in this ratio.

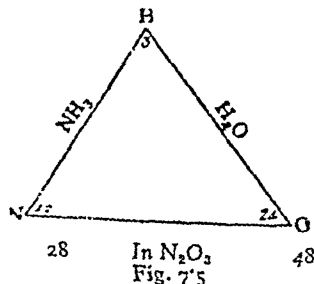


Fig. 7·5

With the development of the idea of combining weight or *equivalent weight as the number of parts by weight of the element which combine with 8 parts by weight of oxygen*, or 1·008 parts by weight of hydrogen, the law is termed as the Law of Combining Weights and may be stated as follows :

Elements combine with one another only in the proportion of their combining weights or simple multiples (or sub-multiples) of them.

For example, equivalent weights of sulphur and oxygen are 16 and 8 respectively. Whenever sulphur and oxygen combine, they will do so in the ratio 16 : 8 or small multiples of these. In SO_2 and SO_3 these ratios have actually been found to be small multiples of the ratio 16 : 8.

Example 4. *Phosphine (PH_3) contains 91·1% of phosphorus and 8·9% of hydrogen ; water (H_2O) contains 88·8% of oxygen and 11·2% of hydrogen ; and P_4O_6 contains 56·4% of phosphorus and 43·6% of oxygen. Show without using the atomic weights that the data illustrate the law of reciprocal proportions.*

(*Nagpur Pre-University 1971*)

% of phosphorus in phosphine $=91·1$

,, hydrogen ,, ,, $=8·9$

Wt. of phosphorus which combines with 1 gm. of hydrogen in phosphine $=\frac{91·1}{8·9}=10·236$ gm.

% of oxygen in water $=88·8$

,, hydrogen ,, ,, $=11·2$

Wt. of oxygen which combines with 1 gm. of hydrogen in water $=\frac{88·8}{11·2}=7·93$ gm.

Ratio between the weights of phosphorus and oxygen which comine with a fixed wt. of hydrogen $(=1 \text{ gm.})=\frac{10·236}{7·93}$

$$=\frac{1·290}{1} \quad ...(i)$$

Ratio between the weights of phosphorus and oxygen which actually combine in $P_4O_6=\frac{56·4}{43·6}$

$$=\frac{1·293}{1} \quad ...(ii)$$

We find that weights of phosphorus and oxygen which combine with a fixed weight of hydrogen [ratio (i)] are the same as the weights of phosphorus and oxygen which actually combine [ratio (ii)]. This illustrates the law of reciprocal proportions.

Example 5. *Nitrous oxide contains 36·3 per cent of oxygen by weight, water contains 88·8 per cent of oxygen by weight, and ammonia contains 82·2 per cent of nitrogen by weight. Show that this data illustrate the Law of Combining Weights.*

Percentage of oxygen in water $= 88{\cdot}8$
,, ,, ,, hydrogen in ,, $= 100 - 88{\cdot}8 = 11{\cdot}2$

i.e., 88·8 parts by weight of oxygen combine with 11·2 parts by weight of hydrogen.

Eq. wt. of oxygen from this $= \frac{88{\cdot}8}{11{\cdot}2} \times 1{\cdot}008 = 8$

Percentage of nitrogen in ammonia $= 82{\cdot}2$
,, ,, hydrogen ,, $= 100 - 82{\cdot}2 = 17{\cdot}8$

i.e., 82·2 parts by weight of nitrogen combine with 17·8 parts by weight of hydrogen.

Eq. wt. of from nitrogen this $= \frac{82{\cdot}2}{17{\cdot}8} \times 1{\cdot}008 = 4{\cdot}66$

Percentage of oxygen in nitrous oxide $= 36{\cdot}3$
,, ,, nitrogen ,, ,, $= 100 - 36{\cdot}3 = 63{\cdot}7$

No. of parts by weight of nitrogen that will combine with one equivalent of oxygen $(= 8) = \frac{63{\cdot}7}{36{\cdot}3} \times 8 = 14{\cdot}04$

Now 14·04 is almost exactly three times 4·66, *i.e.*, three times equivalent of weight of nitrogen. Or the equivalent of oxygen combines with a *simple multiple* of the equivalent of nitrogen.



Joseph Louis Gay Lussac
(1778—1850)
A French chemist and physicist; his law of combining volumes of gases is one of his most famous contributions of science.

This illustrates the Law of Equivalent or Combining Weights.

6. Gay Lussac's Law of Gaseous Volumes.—The law of gaseous volumes as stated by Gay Lussac, a French chemist, in 1809 states: "*Whenever gases react, they always do so in volumes which bear a simple ratio (i) to one another, (ii) to the volumes of the products, if gaseous. All measurement of volumes being made under similar conditions of temperature and pressure.*

For example, in the following chemical reactions the various volumes of reactants and products are found to be in simple ratio without a single exception.

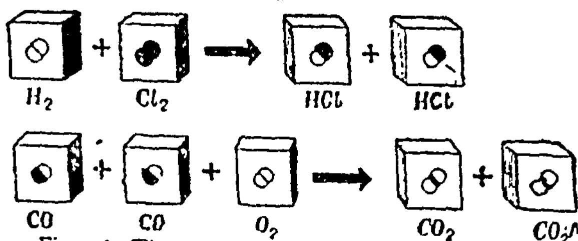
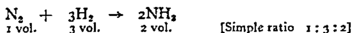
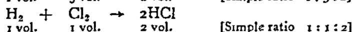


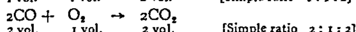
Fig. 7·6—The combining volumes of certain gases.



$N_2 + 3H_2 \rightarrow 2NH_3$
1 vol. 3 vol. 2 vol. [Simple ratio 1 : 3 : 2]



$H_2 + Cl_2 \rightarrow 2HCl$
1 vol. 1 vol. 2 vol. [Simple ratio 1 : 1 : 2]



$2CO + O_2 \rightarrow 2CO_2$
2 vol. 1 vol. 2 vol. [Simple ratio 2 : 1 : 2]

These illustrate the truth of Gay Lussac's Law. This law is purely experimental like other laws of chemical combination. It, however, differs from others in the fact that while others follow as corollaries from the Atomic and Molecular theories (*see* Chapter 8), this does not.

QUESTIONS AND PROBLEMS

Essay type Questions :

1. State and illustrate the following laws of chemical combination :

(*a*) (*i*) Law of Definite Proportions, and

(*ii*) Law of Gaseous Volumes

(*Delhi H.S. 1970, 69, 67 ; Chandigarh 1970*)

(*b*) The Law of Conservation of Mass and the Law of Multiple Proportions. (*Punjab Pre-Univ. 1971, 69 , Delhi H S. 1969, 67 ; Chandigarh 1970*)

2 State and illustrate the Laws of Chemical Combination with suitable examples. (*Nagpur Pre-University 1971*)

3 Explain the Law of Reciprocal Proportions or the Law of Equivalent or Combining Weights with one example of its importance in chemistry. (*Nagpur Pre-University 1971*)

4 *Hydrogen peroxide and water contain 5·93% and 11·2% of hydrogen* respectively. Which law of chemical combination is illustrated by these figures ? State the law. (*All India H.S. 1966 ; Bihar 1966*)

Law of Constant Proportions :

5. State the Law of Definite Proportions and of Multiple Proportions. Outline suitable experiments by which one of the law may be verified. (*Delhi H S. 1961, 60*)

6 Weight of copper oxide obtained by treating 1·59 gm. of metallic copper with nitric acid and subsequent ignition was 1·99 gm.

In another experiment the weight of metallic copper obtained by passing a current of hydrogen over 2·12 gm. of heated cupric oxide was found to be 1·694 gm.

Are these figures in accordance with the Law of Constant Proportions ?

Law of Multiple Proportions :

7. (*a*) Explain and illustrate the Law of Multiple Proportions. How can the truth of this law be verified in the laboratory ? (*U.P Board Inter. 1964*)

[illegible] n at N.T.P. [illegible] of nitrogen [illegible] of Multiple [illegible]

(*U.P. Board Inter. 1964*)

8. Elements *A* and *B*, form two different compounds In one 0·579 gram of *A* is combined with 0·422 gram of *B* , in the other 0·179 gram of *A* is combined with 0·261 gram of *B*. Show that this data illustrate the law. (*Punjab Pre-Univ. 1969*)

9. Three oxides of iron have the following composition :

(i)	(ii)	(iii)
Fe=77·78%	Fe=70·0%	Fe=72·42%
O=22·22%	O=30·0%	O=27·58%

Show how they illustrate the Law of Multiple Proportions :
(*I.I.T. Admission Test 1963*)

10. A metal forms two oxides. One contains 46·67% of the metal and the other 63·94% of the metal. Show that these results are in accordance with the Law of Multiple Proportions. (*Bombay First Year Science 1963*)

11. Elements A and B combine to form two different compounds X and Y.

0·3 g. of A+ 0·4 g. of B → 0·7 g. of X

18·0 g. of A+48·0 g. of B → 66·0 g. of Y.

Show that the Law of Multiple Proportions is illustrated by these data.
(*Punjab Pre-Univ. 1970*)

12. Elements X and Y form two different compounds. In the first 0·324 g. of X is combined with 0·471 g. of Y. In the second 0·117 g. of X is combined with 0·509 g. of Y. Show that these data illustrate the Law of Multiple Proportions. (*Punjab Pre-Univ. 1971*)

13. Copper gives two oxides. On heating one gm. of each in hydrogen we get 0·888 gm. and 0·798 gm. of the metal. Show that the results are in agreement with the Law of Multiple Proportions. (*Delhi H.S. 1965*)

Law of Reciprocal Proportions :

14. Carbon dioxide contains 27·27% of carbon ; carbon disulphide contains 15·79% of carbon and sulphur dioxide contains 50% of sulphur. Illustrate the law of reciprocal proportions.

Law of Combining or Equivalent Weights :

15. Hydrogen sulphide contains 5·88% of hydrogen, water contains 11·11% of hydrogen, sulphur dioxide contains 50% of sulphur.

Show that these figures illustrate the law of combining weights.
(*I.I.T. Admission Test 1962*)

16. Ammonia contains 17·65% hydrogen, water contains 11·11% of hydrogen and nitrogen trioxide contains 36·84% nitrogen.

Show that these figures illustrate the law of equivalent weight.
(*I.I.T. Admission Test 1964*)

17. 0·14 gm. of an element A combines with 0·16 gm. of the element B ; also 0·05 gm. of another element C combines with 0·35 gm. of A. Again it is found that 0·2857 gm. of C combined with 2·2857 gm. of B.

Show that the results are in agreement with the law of equivalent proportions. (*Delhi H.S. 1967*)

18. Explain giving examples, Gay Lussac's law of gaseous volumes. Does this law follow as a corollary from the atomic theory ?

19. Write a short note on the Law of Conservation of Mass.
(*Delhi H.S. 1970*)

Test Your Understanding

20. Fill in the blanks :

(i) Matter can neither be......nor......as a result of any......

(ii) A chemical compound is always found to be made up of......combined together in the......by......

(iii) If two elements A and B combine to give two or more......, then the weights of A which combine with......bear......to one another.

(*iv*) Weights of two elements A and B which......with a fixed weight of...., are either the same or simple multiples of .....which combine with each other.

(*v*) Elements combine with one another only in the proportions of their......or simple......or......of them.

(*vi*) Whenever gases react, they always do so in volumes which bear a simple ratio (*a*) ....., (*b*) ....., if gaseous.

KEY

(*i*) created, destroyed, chemical change. (*ii*) the same elements, same proportion, weight. (*iii*) compounds, a fixed weight of B, a simple ratio. (*iv*) separately combine, the third element C, the weights of A and B. (*v*) combining weights, multiples, sub-multiples, (*vi*) to one another, volumes of *products*.

ANSWERS

4. Law of Multiple Proportions. Weights of oxygen which combine with a fixed weight of hydrogen are in a simple ratio 2 : 1.

6. Percentage of Cu in two samples=79·89 and 79·91 respectively.

7. Wts. of oxygen which combine with a fixed weight of nitrogen are in ratio 1 : 2.

8. Wts. of B combining with fixed weight of A are in the ratio 1 : 2.

9. Wts. of oxygen which combine with a fixed weight of iron are in the ratio 6 : 9 : 8.

10. Wts. of oxygen which combine with a fixed weight of the metal are in the ratio 2 : 1.

11. Weights of B which combine with a fixed weight of A are in the ratio 1 : 2.

12. Weights of Y which combine with a fixed weight of X are in the ratio 1 : 3.

13 Wts. of copper which combine with a fixed weight of oxygen are in the ratio 2 : 1.

14. Wts. of S and O which combine with a fixed weight of carbon (=1, say) are 5·33 and 2·667 respectively.

These weights and the weights of S and O which combine with each other (50 and 50) bear a simple ratio $\frac{5.333}{2.667} : \frac{50}{50} :: 2 : 1$.

15. One equivalent weight of sulphur (=16) combines with two equivalent weights of oxygen (=16).

16. One equivalent weight of N (=4·665) combines with one equivalent weight of oxygen (=8).

17. Weights of B and C which separately combine with a fixed weight of A are the same as the weights of B and C which combine with each other.

STRUCTURE OF MATTER

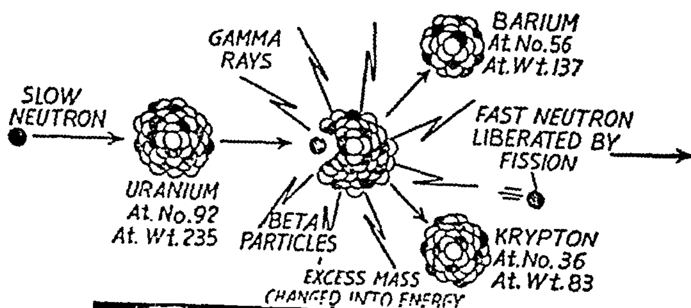
BREACHING THE WALL

THE UNKNOWN

SCIENCE

ATOMIC THEORY

NUCLEAR FISSION



(*v*) Recent developments have enabled us to alter a few types of atoms.

4. **Atomic-Molecular Theory.**—Having made a distinction between atoms and molecules, let us state the atomic-molecular theory. According to this :

(*i*) Ultimate particles of matter are molecules.

(*ii*) Molecules in turn are made up of one or more atoms which are identical in the case of molecules of elements and dissimilar in the case of molecules of compounds.

(*iii*) Molecules of the same substance are alike.

(*iv*) Molecules of different substances are different.

(*v*) The mass of the molecule (molecular weights) is the sum of the masses of its component atoms (atomic weights).

(*vi*) A molecule is the smallest particle of matter that still retains the properties of the original substance.

(*vii*) Chemical reactions involve a redistribution of atoms among the reacting molecules resulting in the formation of new molecules.

5. **Dalton's Atomic Theory and Laws of Chemical Combination.**—We have already seen what drastic changes Dalton's atomic theory [illegible] the modern chemist. If it is still [illegible] lue to the fact that various laws of ch[illegible] as corollaries from it as given below :

(*i*) Law of Conservation of mass follows from the postu- [illegible]

(*ii*) Law of Constant Proportions also follows from postulates (*ii*) and (*iv*) of Dalton's atomic theory as follows :

Let x atoms of an element A (at. wt.$=a$) combine with y atoms of another element B (at. wt.$=b$) to form a molecule of a compound A_xB_y (mol. wt.$=ax+by$). Percentages of A and B in the compound A_xB_y are $\frac{ax}{ax+by}\times 100$ and $\frac{by}{ax+by}\times 100$ respectively.

According to atomic theory a compound is formed by the [illegible] are [illegible] sess [illegible]

Now a, b, x and y being all fixed, the above percentages of A and B in A_xB_y are definite and invariable. This is the *Law of Definite Proportions.*

(*iii*) **Law of Multiple Proportions** follows from postulates (*ii*) and (*iv*) as under :

Let two elements, A (at.wt.$=a$) and B (at.wt.$=b$) combine to form two compounds A_xB_y and A_cB_d. The weights of A and B which combine together are in the ratio :

$$ax : by \quad \text{or} \quad a : \frac{y}{x} \times b \text{ in } A_xB_y$$

$$\text{and} \qquad ac : bd \quad \text{or} \quad a : \frac{d}{c} \times b \text{ in } A_cB_d$$

Weights of B which combine with a fixed weight of A ($=a$) bear a ratio $\frac{y}{x} . b : \frac{d}{c} . b :: cy : dx$ { Cancelling b from both sides ; this being a constant [Postulate (*ii*)].

Now c, d, x and y are all small whole numbers [Postulale (*iv*)]. The ratio $cy : dx$ is, therefore, a simple ratio. This is the *law of multiple proportions.*

(*iv*) **Law of Reciprocal Proportions** follows from postulates (*i*) and (*iv*).

Let m atoms of A and n atoms of B separately combine with p atoms of C to give the compounds A_mC_p and B_nC_p respectively. Further let x atoms of A combine with y atoms of B when they combine together to form A_xB_y.

According to postulate (*iv*) of Dalton's atomic theory, the ratio (*i*) m/p, (*ii*) n/p, and (*iii*) x/y are all simple atomic ratios.

Dividing (i) by (*ii*), m/n is also a simple ratio and must be simply related to another simple ratio x/y, *i.e.*,

m/n and x/y are either equal or simple multiples. ...(*i*)

Let a, b and c be the atomic weights of A, B and C respectively. Then

(*i*) Weights of A and B which combine with a fixed weight of C=(cp) in A_nC_p and B_nC_p are am and bn respectively.

(*ii*) Weights of A and B which combine with each other in A_xB_y are ax and by respectively.

According to the Law of Reciprocal Proportions, the ratios am/bn and ax/by are either equal or simple multiples of each other.

We have already proved [*See* (*i*) above] that m/n and x/y are either equal or simple multiples. Multiplying both by a/b, we get am/bn and ax/by are either equal or simple multiples. This is the *law of reciprocal proportions.*

QUESTIONS

Essay-type Questions

1. Write a short note on Dalton's Atomic Theory.

2. Write a short note on Dalton's Atomic Theory together with the evidence on which it is based. In what respects has it been modified by modern researches ? (*U.P. Board Inter.* 1964 ; *Punjab Pre-Univ.* 1962 ; *Delhi Pre-Medical* 1962)

3. Write a short note on Atomic-Molecular Theory.

4. State Dalton's Atomic Theory and show how the Laws of Chemical Combination can be deduced from it. In what respects has it been necessary to modify this theory? (*Punjab Inter. 1961 ; Delhi Prep 1962 Supp.*)

5. How do you explain various laws of chemical combination on the basis of atomic theory of matter? (*Punjab Pre-Univ. 1971, 70*)

Test Your Understanding

6. Fill in the blanks in the following :

(*i*) Compound atoms of Dalton are termed .. ..by the modern chemist.

(*ii*) Forms of the same element with different atomic weights are called......

(*iii*) Forms of different elements with same atomic weight but different properties are termed .. .

(*iv*) Molecules of the same substance are all......

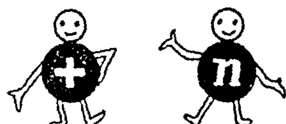
(*v*) Molecule is the smallest particle of matter that .... the properties of the. ....

(*vi*) Chemical reactions involve a .. ..of atoms among the .... resulting in the formation of......

(*vii*) .. ...does not follow as corollary from Dalton's atomic theory.

KEY

(*i*) molecules ; (*ii*) isotopes ; (*iii*) isobars ; (*iv*) alike ; (*v*) still retains, original substance , (*vi*) redistribution, interacting molecules, new molecules ; (*vii*) Gay Lussac's law of gaseous volumes.









Structure of Atoms

1. **Introduction.**—Atoms were believed to be small, hard and indivisible particles for many centuries. It was discovered only fifty years ago that atoms themselves are composed of smaller particles which carry electric charges. The discovery of the components of the atoms and their relative positions inside the atom constitutes one of the most interesting stories in the history of science. In this chapter we shall examine various ideas about the nature of the atom.

2. **Electrons are the essential constituent of all Atoms.**—According to Faraday's laws of electrolysis :

(i) Weight of an ion liberated during electrolysis is proportional to the quantity of electricity passed.

(ii) When the same current passes through different electrolytes, the weights of different elements liberated are proportional to their equivalent weights (which are their atomic weights divided by small whole numbers, *e.g.*, 1, 2, 3, etc.).

The very fact that chemical changes can be produced by electricity suggests a *relationship between matter and electricity* or *an electrical structure of atom*, the ultimate particle of matter. Appearance of products of electrolysis in the ratio of their atomic weights or their definite fractions suggests that *the electrical structure of atoms involves discrete particles of electricity.*

Sir William Crookes (1879) showed that cathode rays are produced on passing electric discharge through different gases at very low pressures in a discharge tube. Cathode rays were made up of negatively charged particles which were named *electrons*. It was found that whatever the nature of the gas or the material of the cathode, the electrons had the same charge to mass (e/m) ratio.

The electrons are also emitted by certain metal filaments when these are strongly heated. Some highly active metals like sodium and potassium emit electrons when exposed to ultra-violet light. All forms of matter emit electrons when exposed to X-rays*. Beta rays emitted by [illegible] 1·85) are also found to be electrons [illegible] any of these methods have been fo[illegible] [illegible]gests that *the electrons are a definite and universal constituent of all atoms.* An electron carries a unit negative charge, but a negligible mass (=1/1846 of the mass of a hydrogen atom).

3. There are protons and neutrons in an atom in addition to electrons.

Since the atom is electrically neutral, the existence of electrons suggests the presence of equal number of positive charges in the atom. The positively-charged particles present in the atom are named *protons.* A proton carries a unit positive charge and possesses a mass equal to one hydrogen atom.

It has been shown that in addition to electrons and protons an atom contains *neutrons.* A neutron has a mass equal to one hydrogen atom and carries no charge.

4. Discovery of Nucleus.—In 1911, Lord Rutherford performed a classic experiment in which he bombarded thin metal

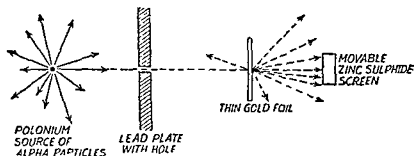


Fig. 9·1—Diagrammatic representation of the Rutherford's Experiment.

foils with high speed α-particles (obtained from a radioactive element). For detection of α-particles, he used a movable screen coated with zinc sulphide. When an α-particle struck the screen a flash of light was seen. He observed that most of the α-particles passed through the foil without deflection while a small proportion of these was scattered or deviated from their path through large angles and a very small fraction recoiled back (*see* Fig. 9·1 and 9·2).

Since α-particles are positively-charged, their deviation from their normal course could only be caused by an approach to something positively-charged situated within the atom. This led Rutherford to his *Nuclear Theory* of the atom. According to this theory,

*X-rays. Invisible and highly penetrating radiations, produced when cathode rays strike a metal target called *anti-cathode*, are called X-rays.

(i) *Whole of the positive charge associated with an atom resides in the central part of the atom known as the Nucleus.* Size

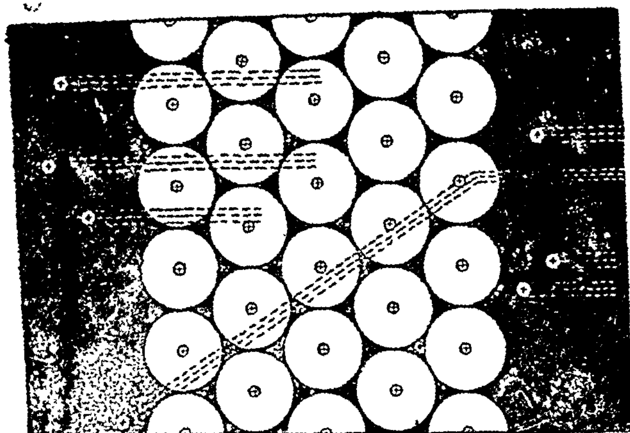


Fig. 9·2—Rutherford's model of the nuclear atom to account for deflection of α-particles.

of the nucleus is very small as compared with the size of the atom. (Diameter of the nucleus is 1/10000 that of the atom). The nucleus is surrounded by hollow space through which α-particles can pass.

(ii) As the atom on the whole is neutral and its central portion is positively charged, electrons must be present in the space surrounding the nucleus.

(iii) The extra-nuclear electrons could not be stationary as otherwise they would be attracted by the positively-charged nucleus and would ultimately fall into it. To have a stable picture of the atom it is assumed that the *extra-nuclear electrons are at relatively great distance from the nucleus and are revolving round the nucleus in closed orbits*, and thus their centrifugal force balances the force of attraction.

(iv) *Nucleus is rigid* and those α-particles which strike against it, recoil back. *It is heavy* since all the protons and neutrons are present in the nucleus. An idea, how small and heavy nucleus is, can be had from the fact that a small box of 1 cubic inch size when packed with gold nuclei, will weigh 4,000 tons.

Bohr Model Atom. In 1913 Bohr pointed out the defects in the above picture of the structure of the atom given by Rutherford. He said that the extra-nuclear electrons being in a state of motion will be gradually losing energy and thus orbits will become smaller and smaller till they fall into the nucleus.

In the light of the modern Quantum Theory of Light he postulated that the electrons are moving only in certain fixed or



Lord Ernest Rutherford (1871—1937)
British physicist; won Nobel Prize for Chemistry in 1908; suggested in 1911 that the atom is made up of a small positively-charged *nucleus* and *outer* electrons—the divisible nuclear atom or the Rutherford atom.



Niels Bohr (1880—1962)
Danish physicist; was awarded Nobel Prize for Physics in 1922, greatly extended the theory of atomic structure by devising an atomic model in 1913 and evolv-*ing theory* of nuclear structure; assisted America in atom bomb research

stationary orbits. *A revolving electron in any* particular orbit is associated with a definite quantity of energy and hence the orbits are known as "Energy Levels."

Further he assumed that electrons are not losing energy constantly. *They lose energy in* quanta or bundles and thus jump from one orbit to the other, depending upon their present energy content. The farther an electron is from the nucleus the greater is the energy associated with it.

This means that under usual circumstances the electrons *move in their fixed or stationary orbits* without any constant loss of energy.

Present Model. Our present picture of an atom is very much like the solar system. *Round* a [illegible] charged nucleus *are the revolving set of electrons.* The atom may be considered to be made up of two parts:

(*a*) The positively-charged [illegible] of the atom is concentrated.

(*b*) The extra-nuclear [illegible]

Nucleus is made up [illegible]:

(i) *Protons*, each [illegible] atom and carrying a [illegible]

(ii) *Neutrons*, each [illegible] carrying no charge.

Atoms differ from each other in their nuclear positive charge and the net positive charge present on the nucleus is known as the **atomic number.** The atomic weight is equal to the sum of protons and neutrons present in the nucleus.

The nucleus has not much to do with the chemical activity of the atom which is due mainly to the extra-nuclear electrons.

The arrangement of these electrons in different orbits is given by Bohr-Bury scheme which can be stated as follows :

(i) *The maximum number of electrons which each orbit can contain is* $2n^2$ *where n gives the number of the orbit.*

Thus number of electrons in the 1st orbit $= 2 \times 1^2 = 2$

" " " 2nd " $= 2 \times 2^2 = 8$, and so on.

(ii) *The maximum number of electrons in the outermost orbit is 8 and in the orbit next to the outermost is 18.*

(iii) *It is not necessary for an orbit to be complete before another commences to be formed. In fact a new orbit begins when the outermost orbit attains 8 electrons.*

(iv) *The outermost orbit cannot have more than 2 electrons and the orbit next to the outermost cannot have more than 9, so long as the next inner orbit in each case has not received the maximum number of electrons as required by rules* (i) *and* (ii).

We have learnt above that :

Atomic weight, W = Protons + Neutrons (both inside the nucleus)

Atomic number, N = Protons (inside) = Electrons (outside)

From this, knowing the atomic weight and atomic number of an atom, we can assign a structure to it as illustrated below :

Structure of Hydrogen. Atomic number of hydrogen is equal to one. There should, therefore, be only one proton present in its nucleus and one electron revolving round it. Further, its atomic weight is also equal to one which means that the number of neutrons ($= W - N$) present in its nucleus is equal to zero. Thus we assign the structure to hydrogen as given in Fig. 9·3.

Structure of Helium. Atomic number, N and atomic weight W, of helium are 2 and 4 respectively. Hence

No. of protons in its nucleus = At. No. = 2.

No. of neutron in its nucleus $= W - N = 4 - 2 = 2$

No. of electrons outside = At. No. = 2.





Fig. 9·3—Atomic structure of hydrogen and helium.

Thus there are 2 protons and 2 neutrons present in the

nucleus of helium while 2 electrons (both in the first orbit) are revolving around the nucleus (*see* Fig. 9·3).

Atomic structures in the case of a few other commoner elements, as deduced from their At. Wt. and At. No., are summarized in the table given below :

Element	At. Wt. =W	At. No. =N	Nucleus contains: *Protons* =N	*Neutrons* =W−N	Extra-nuclear Electrons: *Their Number* =N	*Arrangement in orbits* 1st	2nd	3rd orbit
Lithium	7	3	3	4	3	=2	1	
Beryllium	9	4	4	5	4	=2	2	
Boron	11	5	5	6	5	=2	3	
Carbon	*12*	*6*	*6*	*6*	*6*	*=2*	*4*	
Nitrogen	14	7	7	7	7	=2	5	
Oxygen	16	8	8	8	8	=2	6	
Fluorine	19	9	9	10	9	=2	7	
Neon	20	10	10	10	10	=2	8	
Sodium	23	11	11	12	11	=2	8	1
Magnesium	24	12	12	12	12	=2	8	2
Aluminium	27	13	13	14	13	=2	8	3
Silicon	28	14	14	14	14	=2	8	4
Phosphorus	31	15	15	16	15	=2	8	5
Sulphur	32	16	16	16	16	=2	8	6
Chlorine	35	17	17	18	17	=2	8	7
Argon	40	18	18	22	18	=2	8	8
Tin	118	50	50	68	50 (2, 8, 18, 18, 4)			
Lanthanum	139	57	57	82	57 (2, 8, 18, 18, 9, 2)			
Xenon	131	54	54	77	54 (2, 8, 18, 18, 8)			



LITHIUM
At. No.=3
At. Wt.=7



BERYLLIUM
At. No.=4
At. Wt.=9



BORON
At. No.=5
At. Wt.=11



CARBON
At. No =6
At. Wt.=12



NITROGEN
At. No.=7
At. Wt.=14



OXYGEN
At. No.=8
At. Wt.=16



FLUORINE
At. No.=9
At. Wt.=18



NEON
At. No.=10
At. Wt.=20



SODIUM
At. No.=11
At. Wt.=23



MAGNESIUM
At. No =12
At. Wt.=24



ALUMINIUM
At. No.=13
At. Wt.=27



SILICON
At. No.=14
At. Wt.=28

Atoms differ from each other in their nuclear positive charge and the net positive charge present on the nucleus is known as the **atomic number.** The atomic weight is equal to the sum of protons and neutrons present in the nucleus.

The nucleus has not much to do with the chemical activity of the atom which is due mainly to the extra-nuclear electrons.

The arrangement of these electrons in different orbits is given by Bohr-Bury scheme which can be stated as follows :

(i) *The maximum number of electrons which each orbit can contain is $2n^2$ where n gives the number of the orbit.*

Thus number of electrons in the 1st orbit $=2\times 1^2=2$

" " " 2nd " $=2\times 2^2=8$, and so on.

(ii) *The maximum number of electrons in the outermost orbit is 8 and in the orbit next to the outermost is 18.*

(iii) *It is not necessary for an orbit to be complete before another commences to be formed. In fact a new orbit begins when the outermost orbit attains 8 electrons.*

(iv) *The outermost orbit cannot have more than 2 electrons and the orbit next to the outermost cannot have more than 9, so long as the next inner orbit in each case has not received the maximum number of electrons as required by rules* (i) *and* (ii).

We have learnt above that :

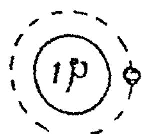
Atomic weight, W = Protons + Neutrons
both inside the nucleus

Atomic number, N = Protons = Electrons
inside outside

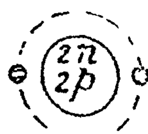
From this, knowing the atomic weight and atomic number of an atom, we can assign a structure to it as illustrated below :

Structure of Hydrogen. Atomic number of hydrogen is equal to one. There should, therefore, be only one proton present in its nucleus and one electron revolving round it. Further, its atomic weight is also equal to one which means that the number of neutrons $(=W-N)$ present in its nucleus is equal to zero. Thus we assign the structure to hydrogen as given in Fig. 9·3.

Structure of Helium. Atomic number, N and atomic weight W, of helium are 2 and 4 respectively. Hence



HYDROGEN
At. Wt. = 1
At. No. = 1



HELIUM
At. Wt. = 4
At. No. = 2

Fig. 9·3—Atomic structure of hydrogen and helium.

No. of protons in its nucleus
= At. No. = 2.

No. of neutron in its nucleus
$=W-N=4-2=2$

No. of electrons outside
= At. No. = 2.

Thus there are 2 protons and 2 neutrons present in the

nucleus of helium while 2 electrons (both in the first orbit) are revolving around the nucleus (*see* Fig. 9·3).

Atomic structures in the case of a few other commoner elements, as deduced from their At. Wt. and At. No., are summarized in the table given below :

Element	At. Wt. $=W$	At. No $=N$	Nucleus contains: *Protons* $=N$	*Neutrons* $=W-N$	Extra-nuclear Electrons: *Their Number* $=N$	*Arrangement in orbits* 1st	2nd	3rd orbit
Lithium	7	3	3	4	3	=2	1	
Beryllium	9	4	4	5	4	=2	2	
Boron	11	5	5	6	5	=2	3	
Carbon	12	6	6	6	6	=2	4	
Nitrogen	14	7	7	7	7	=2	5	
Oxygen	16	8	8	8	8	=2	6	
Fluorine	19	9	9	10	9	=2	7	
Neon	20	10	10	10	10	=2	8	
Sodium	23	11	11	12	11	=2	8	1
Magnesium	24	12	12	12	12	=2	8	2
Aluminium	27	13	13	14	13	=2	8	3
Silicon	28	14	14	14	14	=2	8	4
Phosphorus	31	15	15	16	15	=2	8	5
Sulphur	32	16	16	16	16	=2	8	6
Chlorine	35	17	17	18	17	=2	8	7
Argon	40	18	18	22	18	=2	8	8
Tin	118	50	50	68	50	(2, 8, 18, 18, 4)		
Lanthanum	139	57	57	82	57	(2, 8, 18, 18, 9, 2)		
Xenon	131	54	54	77	54	(2, 8, 18, 18, 8)		



LITHIUM
At. No.=3
At. Wt.=7



BERYLLIUM
At No.=4
At. Wt =9



BORON
At. No.=5
At. Wt.=11



CARBON
At. No.=6
At. Wt.=12



NITROGEN
At. No.=7
At. Wt.=14



OXYGEN
At. No.=8
At. Wt.=16



FLUORINE
At. No.=9
At. Wt.=18



NEON
At. No.=10
At. Wt.=20



SODIUM
At. No.=11
At. Wt.=23



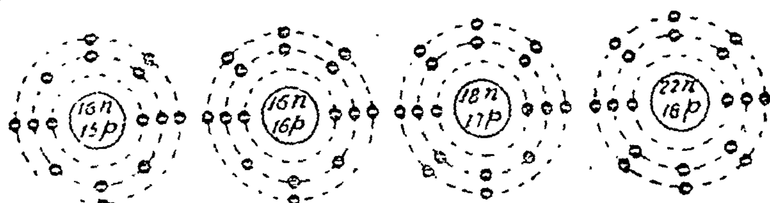
MAGNESIUM
At. No.=12
At. Wt.=24



ALUMINIUM
At. No.=13
At. Wt.=27



SILICON
At. No.=14
At. Wt.=28



PHOSPHORUS At. No.=15 At. Wt.=31 | SULPHUR At. No.=16 At. Wt.=32 | CHLORINE At. No.=17 At. Wt.=35 | ARGON At. No.=18 At. Wt.=40

Fig. 9·4—Atomic structures of elements of first and second short periods.

A Warning. At present it is believed that the *electrons, like light, have a dual particle-wave nature*. In view of the later developments, the whole concept of orbits and energy distribution around the nucleus takes an altogether different form.

At present, electron is not regarded as having a fixed place or an orbit within the atom. It is rather a matter of probability that

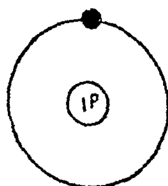


Fig. 9·5—Bohr conception of the hydrogen atom as a proton circled by an electron.



Fig. 9·6—Modern picture of the hydrogen atom as a proton surrounded by a charged cloud in which there is a probability of finding the electron.

the electron is more likely to be found in one place than another. The old Bohr model of the hydrogen atom as having a proton circled by an electron (Fig. 9·5) has now been replaced by the conception of the atom as possessing a proton surrounded by a charged cloud in which there is a probability of finding the electron (shown by shaded volume in Fig. 9·6). In this shading the darker part indicates the greater probability of the electron being found there. As the distance from the proton increases, the shading becomes less intense, indicating that there is less probability of the electron being found there.

The picture of the atom as consisting of a central nucleus with a number of electrons moving round it in definite orbits is misleading. Regarded as purely symbolic, this picture might be justified ; nevertheless, there is always a danger that it may be interpreted too literally.

5 Nuclear Stability.—The forces within the nucleus of the atom are indeed strangely different from the forces encountered elsewhere. Two protons, for example, repel each other ordinarily. But at a distance about 10^{-12} cm. inside the nucleus they attract each other mightily. Inside the tiny world of the nucleus where the density is about 130 million tons/c.c., forces entirely different from gravitation or electrostatic interaction take over.

These enormous forces within the [illegible] of the binding energy. Mass of an atom [illegible] its constituent particles. The difference [illegible] as *mass defect*. The energy equivalent [illegible] tein's energy equation, $E=mc^2$) is the [illegible]

Consider, for example, the helium [illegible] and two neutrons.

Mass of 2 protons	[illegible]
Mass of 2 neutrons	[illegible]
[illegible]	[illegible]

However, actual mass of a helium nucleus is [illegible] amu.

∴ Mass defect in this case = [illegible] amu.

= [illegible] amu.

Energy equivalent to this mass is the binding energy of the nucleus. If two protons and two neutrons were brought together to form the helium nucleus, this much energy will be released. On the other hand, if the helium nucleus was to break up into two protons and two neutrons, so much energy will have to be supplied to it.

SOME MODERN CONCEPTS

Electronic configurations of a few more elements are given in the table.

Element	At. No.	Electron Population: K or 1-shell	L or 2-shell		M or 3-shell			N or 4-shell			
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f
Sodium	11	2	2	6	1						
Argon	18	2	2	6	2	6					
Potassium	19	2	2	6	2	6		1			
Calcium	20	2	2	6	2	6		2			
Scandium	21	2	2	6	2	6	1	2			
Iron	26	2	2	6	2	6	6	2			
Krypton	36	2	2	6	2	6	10	2	6		

7. **Sub-shells and Orbitals.**—*The region in space occupied by an electron is called its* **orbital.** *In reality it is the region where there is high probability of finding the electron.* An orbital can accommodate a maximum of 2 electrons. Orbitals of a principal shell and the electrons that occupy them are arranged in sub-shells. The number of orbitals comprising a sub-shell differs with each type of sub-shell. Thus *s* sub-shell (c ontaining 2 electrons)

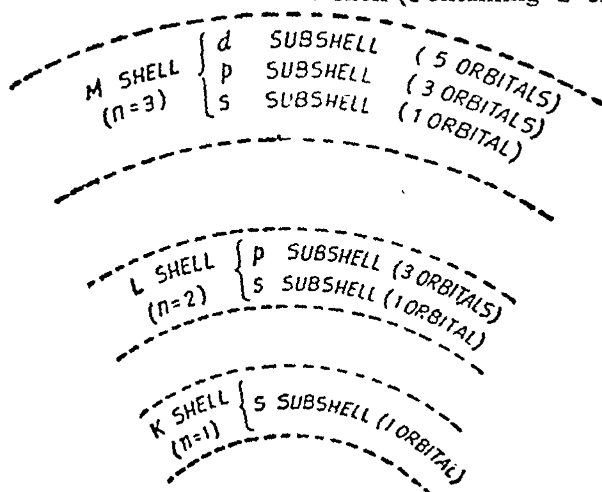


Fig. 9·7—Arrangement of shells, sub-shells and orbitals in an atom (only first three shells shown).

is made up of only one orbital, p sub-shell (containing 6 electrons) is made up of 3 orbitals, d sub-shell (containing [illegible] electrons) is made up of 5 orbitals and f sub-shell (containing 14 electrons) is made up of 7 orbitals.

Adarsh ... Re...
JAIPUR-302...

s orbital is spherically symmetrical while three p-orbitals are dumb-bell shaped and inclined mutually at right angles. These are designated as p_x, p_y and p_z orbitals. These are electron clouds directed in different directions in space (*see* Fig. 9·8).

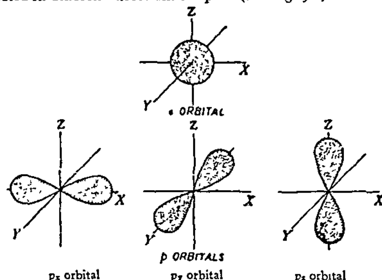
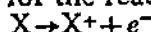


Fig. 9·8—Geometrical representation of the s and p atomic orbitals.

Carbon	$1s^2, 2s^2, 2p^2$	or	$1s^2, 2s^2, 2p_x^1, 2p_y^1$
Nitrogen	$1s^2, 2s^2, 2p^3$	or	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$
Oxygen	$1s^2, 2s^2, 2p^4$	or	$1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

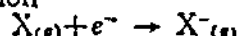
8. Some electron-based Properties of Elements.

(i) Ionization Potential. The firmness with which an electron is held by an atom is a measure of its ionization potential. It is defined as the energy required to pull off an electron from the atom, *i.e.*, energy required for the reaction.



$$X \rightarrow X^+ + e^-$$

(ii) Electron Affinity. Another important factor that determines the chemical property of an atom is its tendency to pick up an additional electron. The measure of this property is the amount of energy that is released when an electron is added to neutral atom, *i.e.*, energy of the reaction

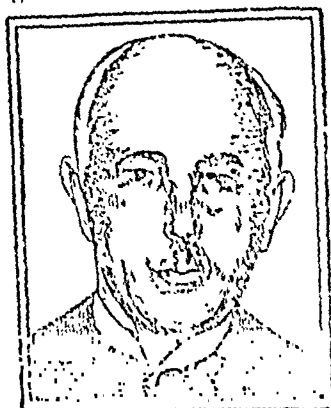


$$X_{(g)} + e^- \rightarrow X^-_{(g)}$$

(iii) Electronegativity. The tendency of an atom in a compound to attract electrons to itself is termed the electronegativity of the atom.

ISOTOPES AND ISOBARS

9. What are Isotopes ?—As a result of researches of Sir J.J. Thomson, William Aston, T.W. Richards, and Frederick Soddy, it was concluded that *not all atoms of a single element have the same weight.* Atoms of the same element, almost identical in chemical



Francis William Aston

(1877 – 1945)

English Physicist : he received the Nobel Prize for Chemistry in 1922 for his work on isotopes.



Frederick Soddy
(1877 – 1956)
English physicist and chemist ; he was elected F.R.S. in 1910 and was awarded Nobel Prize for Chemistry in 1919. He gave the name *isotopes* to different varieties of lead which he discovered in 1913 in radioactive minerals.

properties but differing in atomic mass, are called *isotopes.* The atomic numbers of the isotopes of an element are the same. Isotopes *can, therefore, be defined as forms of the same element having the same atomic number but different atomic weights due to different nuclear structures.*

Atomic weights determined by chemists are only *average weights* of the mixture of isotopes of different elements. This explains the fractional atomic weights of a large number of elements.

10. Isotopes of Hydrogen.—There are three known forms of isotopes of hydrogen, each possessing an atomic number one. The commonest form is the ordinary hydrogen with atomic weight one. It consists of one proton in its nucleus and one electron revolving around it. The second isotope of hydrogen is called *heavy hydrogen* or *deuterium.* It consists of one proton and one neutron in the nucleus with one electron revolving around. Its atomic weight is 2 and it is present in hydrogen gas to the extent of one part in 6,900. The third is a *synthetic* (man made) *isotope*

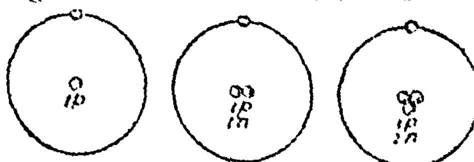


Fig. 9·9 Three isotopes of hydrogen.

called *tritium* with an atomic weight of three. Its nucleus contains one proton and two neutrons with one electron, as before, in its first orbit (or K orbit). Their average atomic weight is 1·008 *amu* (atomic weight unit).

11. **Isotopes of Oxygen.**—The three isotopes of oxygen ($_8O^{16}$, $_8O^{17}$ and $_8O^{18}$) possess atomic weights 16, 17 and 18 respectively, their atomic number being 8 in each case. Each one of these has 8 protons in its nucleus and 8 electrons in the extra nuclear part (2 in the first orbit and 6 in the second orbit). The neutrons present in their nuclei are 8, 9 and 10 respectively as shown in their atomic models given above.

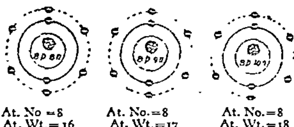


Fig. 9·10—Three isotopes of oxygen.

12. **Isotopes of Chlorine.**—Two isotopes of chlorine ($_{17}Cl^{35}$ and $_{17}Cl^{37}$ each with atomic number=17) have atomic weights of 35 and 37 respectively. Their average atomic weight is 35·457. Nuclear composition of these isotopes can be represented as follows :

At. wt.	*Protons*	*Neutrons*	*Electronic arrangement*
35	17	18	17=2+8+7
37	17	20	the same

13. **Detection of Isotopes.**—When an electric discharge is passed through a gas under low pressure contained in a discharge tube with a perforated cathode, positively charged ions are produced. Rays of these ions pass through the perforated cathode and are termed *positive rays*. These positive rays, if passed through electric and magnetic fields, are deviated from their path. The deviation is proportional to the charge/mass ratio (*e/m*) of these positi[illegible]
mixtu[illegible]
the he[illegible]
path, [illegible]

This is the underlying principle of Aston's mass spectrograph (Fig. 9·11) used for detection of isotopes. The unknown gas is

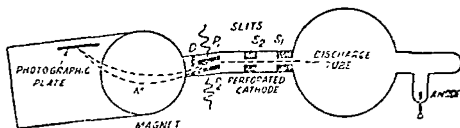


Fig. 9·11—Essential parts of Aston's mass spectrograph.

placed in the discharge tube and the positive rays thus produced are passed through electric and magnetic fields and then allowed to strike a photographic plate. The photographic plate after development is termed mass spectrum since the positions of different lines on it depends on the masses of various ions present in the positive rays. In the mass spectrum—

(*i*) The total number of these lines is the number of isotopes present in the unknown gas.

(*ii*) The relative intensities of these lines give the relative abundance of various isotopes.

(*iii*) From the distances between various lines, the atomic weights of the different isotopes are calculated.

14. **Isobars.**—Several isotopes of different elements (all with different atomic numbers) have the same atomic weights, *e.g.*,

Ar, K, Ca=40 ; Ni, Zn=64 ; Kr, Sr,=86.

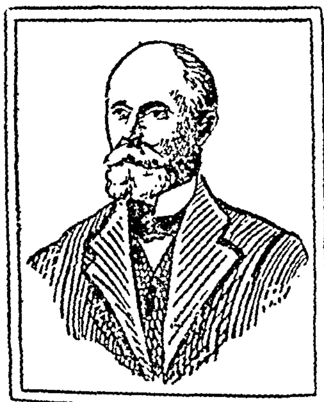
These are called Isobars and are defined *as atoms of different elements with different atomic numbers but identical atomic weights.* They differ from each other in every respect except atomic weights.

RADIOACTIVITY

15. **Discovery.**—In 1896, the French physicist, Henri Becquerel, found that certain uranium minerals emitted penetrating radiations similar to those which Rontgen had discovered. Such substances as uranium mineral are called *radioactive* and the property is called *radioactivity.*



Mme. Marie Curie (1867—1934)
Polish physicist and chemist ; famous for her dicovery of radium ; won Nobel Prize for Chemistry in 1911 and shared Nobel Prize for Physics in 1903 with her husband and Becquerel. She belongs to a family which won five Nobel Prizes in two generations.



Antoine Henri Becquerel
(1852—1908)
French physicist ; he was a Nobel Prize winner for Physics in 1903 with the Curies. In 1896 he discovered the rays named after him, which are given by uranium salt.

Marie Curie, with her husband, Pierre Curie, separated from

pitchblende (a uranium mineral) an element many times more active than uranium. This was the well-known radium.

Fig. 9·12—Different types of radiations. Fig. 9·13—Nature of α-, β- and γ-rays

16. The Nature of Radioactivity.—Rutherford and Soddy found that uranium and radium atoms were not stable but disinte- [illegible]

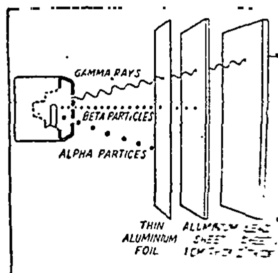


Fig. 9·14—Penetrating powers of α-, β- and γ-rays

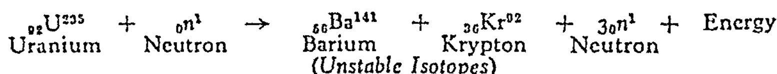
them consisting of three different types.

(1) **Alpha particles.** These are helium nuclei (mass=4) each carrying two units of positive charge. These move with a velocity of [illegible] to 20,000 miles per second. Their penetrating power is not as great as that of other types of radiations. [illegible] sheet of [illegible] aluminium foil [illegible] them. They [illegible] a gas [illegible] from the [illegible]

(*ii*) Beta particles. These are identical with electrons moving with a velocity of 60,000 to 1,60,000 miles per second. Their penetrating power is much greater than that of α-particles but their ionizing power is less.

(*iii*) Gama rays. These seem to be high-energy X-rays caused by impacts of β-particles on surrounding matter. These are electro-magnetic in nature and are most penetrating.

17. **Nuclear Fission.**—In the case of radioactive elements the nucleus is constantly disintegrating to give out α- or β-particles. It can, however, be artificially disintegrated with high speed α-particles or protons but slow neutrons have proved to be better bullets. For example, when U-235 is bombarded with slow neutrons, these are captured by the nucleus. The additional neutron makes the nucleus very unstable and it splits up into two parts of almost equal mass. *This breaking up of the nucleus into two parts of almost equal mass is called* Nuclear Fission. The equation for the fission of U-235 is :



$$_{92}U^{235} + {_0}n^1 \rightarrow {_{56}}Ba^{141} + {_{36}}Kr^{92} + 3{_0}n^1 + \text{Energy}$$

Uranium, Neutron, Barium, Krypton (*Unstable Isotopes*), Neutron

The mass of products is slightly less than 236 while mass of the reactant is slightly greater than 236. The difference of mass (about 0·2 *amu*) is converted into energy according to the equation :

$$E = m \times c^2$$

Energy = Mass × Vel. of light

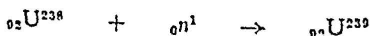
18. **The Atomic Bomb.**—The fast neutrons obtained by neuclear fission of U-235, when slowed by a graphite moderator can start the fission of other U-235 nuclei. Thus rapidly accelerating chain reaction is set up and the atoms undergo fission almost instantaneously with the liberation of tremendous energy which causes havoc. This is the underlying principle of an atom bomb first used at Hiroshima and Nagasaki in Japan. It has been found now that plutonium can be used in place of U-235 in atomic bombs.



Enrico Fermi
(1901–)

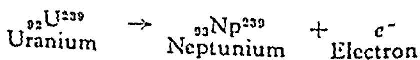
Indian physicist. He won Nobel Prize for Physics in 1938 for research on artificial radioactivity. He was the first to bombard nuclei of heavy elements with neutrons for transmutation.

19. **The Man-made Elements.**—In 1934 Enrico Fermi bombarded U-238 with neutrons and succeeded in converting it into a new heavier isotope.



$$_{92}U^{238} + {_0}n^1 \rightarrow {_{92}}U^{239}$$

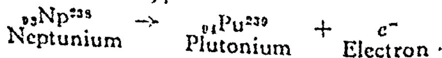
Later, it was found that the new isotope is unstable and loses an electron, thus yielding a new element *neptunium* (Np) with at. no. 93.



$$_{92}U^{239} \rightarrow {_{93}}Np^{239} + e^-$$

Uranium → Neptunium + Electron

Neptunium is unstable and loses a second electron forming another relatively stable man-made element, plutonium (Pu) with an at. no. of 94.



$$_{93}Np^{239} \rightarrow {_{94}}Pu^{239} + e^-$$

Neptunium → Plutonium + Electron

Nuclear scientists did not stop there in the building of new elements. In the course of their work on atomic energy, they have already created the elements given below :

At. No.	Name	Symbol	At. No.	Name	Symbol
95	Americium	Am	101	Mendelevium	Md
96	Curium	Cm	102	Nobelium	No
97	Berkelium	Bk	103	Lawrencium	Lr
98	Californium	Cf	104	Kurchatovium	Ku
99	Einsteinium	Es	105	Hahnium	Ha
100	Fermium	Fm	112	Eka-mercury	Not settled

QUESTIONS

Essay-type Questions

1. Write a short note on the structure of the atom.
(Rajasthan Inter. 1962 ; U.P. Board 1962 ; Delhi H.S. 1965, 62, 61 ; Punjab Pre-University 1962 ; Delhi Pre-Medical 1963)

2. Explain the terms : (*a*) Electron, (*b*) Neutron, (*c*) Atomic number, (*d*) Covalency, and (*e*) Nuclear charge.

The nucleus of an atom of an element consists of twelve neutrons and eleven protons. What is the atomic weight and the electrovalency of the element ? Give the electronic structure of (*i*) Helium atom, (*ii*) Carbon atom.

[Ans. At. wt.=23 ; Electrovalency=1] *(Punjab Inter. 1962)*

3. (*a*) Name the three important particles which constitute the atom. What are their essential characteristics ?

(*b*) Give the atomic structure of the following elements

(*i*) Carbon (At. Wt.=12 ; At. No.=6)

(*ii*) Oxygen (At. Wt.=16 ; At. No.=8)

(*iii*) Sodium (At. Wt.=23 ; At. No.=11)

(*iv*) Chlorine (At. Wt.=35 ; At. No.=17)

Comment on the valency behaviour of the elements you select.
(Punjab Inter. 1960)

(*c*) Using orbital symbols write the electronic configuration of an atom of sodium (At. No.=11). *(Punjab Pre-Univ. 1971)*

(*d*) How many electrons are there in (*i*) hydrogen atom, and (*ii*) chlorine atom (At. No.=17) ? How are they arranged ? *(I.I.T. Admission Test 1969)*

4. Distinguish, giving examples, between
(*a*) Isotopes and Isobars.
(*b*) Atomic weight and Atomic number.
(*c*) Ionization potential, Electron affinity and Electronegativity.

5. (*a*) Give the essential features of the Bohr s model of the atom.
(*b*) Explain the difference between orbit and orbital.
(*c*) Describe the ...

7. Name the elements that correspond to each of the following electron configurations :

(a) $1s^2$ (b) $1s^2, 2s^1$ (c) $1s^2, 2s^1, 2p^1$

(d) $1s^2, 2s^2, 2p^3$ (e) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$.

(Punjab Pre-Univ. 1969)

8. Distinguish between shells, sub-shells and orbitals. Give the electron distribution into the available orbits in the following elements :

Element	Na	Mg	Al	Si	P	S	Cl	Ar
At. No.	11	12	13	14	15	16	17	18

9. What is radioactivity ? Give properties of the different types of rays given out by radioactive substances.

(Chandigarh H.S. 1970 ; Punjab Pre-Univ. 1971)

10. Write short notes on :

(a) Aston's Mass Spectrograph ; (b) Hund's Rule ;

(c) Nuclear fission ; (d) Atomic bomb ;

(e) The Man-made elements.

Test Your Understanding

11. Fill in the blanks in the following :

(i) 18 neutrons and 17 protons are present in the nucleus of the atom of an element.

Its atomic weight is......and valency is......

(ii) 10 protons and 10 neutrons are present in the nucleus of the atom of an element.

Its atomic weight is......, atomic number is......and valency is......

(iii) s orbital is......while p orbitals are......

(iv) Energy necessary for the reaction ($X \rightarrow X^+ + e^-$) is termed......

12. Tick the correct answer from the alternatives given in various questions :

(a) An atom contains 14 neutrons, 13 electrons and 13 protons. Its atomic number, mass number and valency (in that order) are :

(i) 13, 26, 5 ; (ii) 14, 26, 3 ; (iii) 14, 27, 0 ;

(iv) 13, 27, 3 ; (v) 14, 40, 5.

(b) In the nth electron shell the number of electrons is

(i) $2n^2$; (ii) $n-1$; (iii) $2n$; (iv) n ; (v) n^2.

(c) The addition of a neutron to the nucleus of an atom would

(i) change the chemical nature of the atom.

(ii) increase the atomic weight of the atom.

(iii) alter the number of charges in the nucleus.

(iv) increase the atomic number of the atom.

(v) reduce the number of electrons.

(d) The atomic number of an element does not determine the

(i) number of protons in the nucleus.

(ii) position in the periodic table.

(iii) number of neutrons in the nucleus.

(iv) number of electrons around the nucleus.

(v) valence.

KEY

11. (i) 35, 1 (electronegative) ; (ii) 20, 10, 0 ;
(iii) spherical, dumb-bell shaped ; (iv) ionization energy.

12. (a)—(iv) ; (b)—(i) ; (c)—(ii) ; (d)—(iii).

NATURE OF BONDS

IONIC BOND	COVALENT BOND	
Na Cl → Na^+ Cl BY TRANSFERENCE OF ELECTRONS	H H BY MUTUAL SHARING OF ELECTRONS (OLD VIEW)	H : H BY OVERLAP OF ELECTRON CLOUDS (MODERN VIEW)

10

Theory of Chemical Bonding

1. **Introduction.**—Chemistry, as we know, is the study of the composition of various objects of matter and the changes in composition which they undergo. One of the most exciting endeavours of the inquisitive mind of the chemist has been to understand the basic units of matter that make up the material world around. He has succeeded in finding out that such units are molecules consisting of atoms. Even the inside of the atom is no longer a secret to him (Chapter 9).

The next question before him was why and how are the atoms held together into the molecules. A convincing answer to this forms the content of our present chapter, giving the nature of chemical bonding.

ELECTRONIC THEORY OF VALENCY

2. **General.**—The simpler definition of valency as the combining capacity of an atom could not explain the valency of carbon *in* CH_4, C_2H_6 *and* C_2H_4. *To explain the formation of such compounds* the electronic theory of valency was put forward from a study of the electronic configuration of noble gases (*see* table below) and other elements (*see* page 1·78).

Electronic Structure of Noble Gases

Noble Gas	*At. No.*	*Electronic arrangement*
Helium	2	2
Neon	10	2, 8
Argon	18	2, 8, 8
Krypton	36	2, 8, 18, 8
Xenon	54	2, 8, 18, 18, 8
Radon	86	2, 8, 18, 32, 18, 8

7. Name the elements that correspond to each of the following electron configurations :

(a) $1s^2$ (b) $1s^2, 2s^1$ (c) $1s^2, 2s^1, 2p^1$
(d) $1s^2, 2s^2, 2p^3$ (e) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$.

(*Punjab Pre-Univ. 1969*)

8. Distinguish between shells, sub-shells and orbitals. Give the electron distribution into the available orbits in the following elements :

Element	Na	Mg	Al	Si	P	S	Cl	Ar
At. No.	11	12	13	14	15	16	17	18

9. What is radioactivity ? Give properties of the different types of rays given out by radioactive substances.

(*Chandigarh H.S. 1970 ; Punjab Pre-Univ. 1971*)

10. Write short notes on :
(a) Aston's Mass Spectrograph ; (b) Hund's Rule ;
(c) Nuclear fission ; (d) Atomic bomb ;
(e) The Man-made elements.

Test Your Understanding

11. Fill in the blanks in the following :

(i) 18 neutrons and 17 protons are present in the nucleus of the atom of an element.

Its atomic weight is......and valency is......

(ii) 10 protons and 10 neutrons are present in the nucleus of the atom of an element.

Its atomic weight is......, atomic number is......and valency is......

(iii) *s* orbital is......while *p* orbitals are......

(iv) Energy necessary for the reaction ($X \rightarrow X^+ + e^-$) is termed......

12. Tick the correct answer from the alternatives given in various questions :

(a) An atom contains 14 neutrons, 13 electrons and 13 protons. Its atomic number, mass number and valency (in that order) are :
(i) 13, 26, 5 ; (ii) 14, 26, 3 ; (iii) 14, 27, 0 ;
(iv) 13, 27, 3 ; (v) 14, 40, 5.

(b) In the *n*th electron shell the number of electrons is
(i) $2n^2$; (ii) $n-1$; (iii) $2n$; (iv) n ; (v) n^2.

(c) The addition of a neutron to the nucleus of an atom would
(i) change the chemical nature of the atom.
(ii) increase the atomic weight of the atom.
(iii) alter the number of charges in the nucleus.
(iv) increase the atomic number of the atom.
(v) reduce the number of electrons.

(d) The atomic number of an element does not determine the
(i) number of protons in the nucleus.
(ii) position in the periodic table.
(iii) number of neutrons in the nucleus.
(iv) number of electrons around the nucleus.
(v) valence.

KEY

11. (i) 35, 1 (electronegative) ; (ii) 20, 10, 0 ;
(iii) spherical, dumb-bell shaped ; (iv) ionization energy.

12. (a)—(iv) ; (b)—(i) ; (c)—(ii) ; (d)—(iii).

NATURE OF BONDS

IONIC BOND

10

BY TRANSFERENCE OF ELECTRONS

COVALENT BOND

BY MUTUAL SHARING OF ELECTRONS (OLD VIEW)

BY OVERLAP OF ELECTRON CLOUDS (MODERN VIEW)

Theory of Chemical Bonding

1. **Introduction.**—Chemistry, as we know, is the study of the composition of various objects of matter and the changes in composition which they undergo. One of the most exciting endeavours of the inquisitive mind of the chemist has been to understand the basic units of matter that make up the material world around. He has succeeded in finding out that such units are molecules consisting of atoms. Even the inside of the atom is no longer a secret to him (Chapter 9).

The next question before him was why and how are the atoms held together into the molecules. A convincing answer to this forms the content of our present chapter, giving the nature of chemical bonding.

ELECTRONIC THEORY OF VALENCY

2. **General.**—The simpler definition of valency as the combining capacity of an atom could not explain the valency of carbon in CH_4, C_2H_6 and C_2H_4. To explain the formation of such compounds the electronic theory of valency was put forward from a study of the electronic configuration of noble gases (*see* table below) and other elements (*see* page 1·78).

Electronic Structure of Noble Gases

Noble Gas	*At. No.*	*Electronic arrangement*
Helium	2	2
Neon	10	2, 8
Argon	18	2, 8, 8
Krypton	36	2, 8, 18, 8
Xenon	54	2, 8, 18, 18, 8
Radon	86	2, 8, 18, 32, 18, 8

3. **The Lewis-Langmuir Concept of Stable Configuration.**—There are eight electrons in the outermost orbit of all noble



Gilbert Newton Lewis
(1875–1946)
American chemist; with Langmuir developed the atomic theory named after them; also produced a theory of valency.



Irving Langmuir
(1881–1957)
American chemist; won Nobel Prize for Chemistry in 1932; with Lewis evolved an atomic theory.

gases except helium whose electrons (=2) are all in orbit 1. These enter into practically no reactions and form no compounds. The condition of inactivity or maximum stability is evidently associated with their particular electronic arrangement. *The electronic arrangement in which eight electrons are present in the outermost orbit is called* **stable configuration.** Of course, if the outermost orbit is the first one (as in Helium), the number is *two*.

In the case of all other elements which show chemical activity the outermost orbits are found *to be incomplete*. From this Lewis and Langmuir stated that in all cases *there is a general tendency for elements to enter into chemical reactions in such a way as to acquire that stable configuration.* It would not be exaggeration to say that elements react with the main object to attain a stable *configuration*.

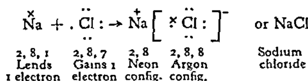
4. **Electronic Theory of Valency.**—The electrons present in the outermost orbit of an atom determine its valency and are therefore, called the **valency electrons.** If the valency electrons be removed, the remainder of the atom is called the **kernel** of the atom.

Formation of chemical compounds from elements involves either transference of the valency electrons of one element to the outermost orbit of the other or sharing of valency electrons of the two atoms. In either case **chemical bond** is set up and as a result of it both the atoms acquire stable configuration.

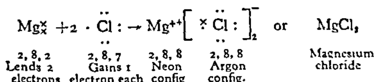
Thus valency of an atom, according to the electronic theory of valency, is the number of electrons it can lend, borrow or share. The lending atom is called electro-positive while a borrowing atom is called electro-negative.

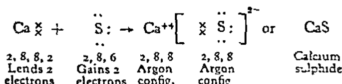
5. **Three Modes of Valency.**—This tendency of the atom can be satisfied in three different ways and corresponding to these three ways there are three modes of valency.

(i) Electrovalency (By transference of electrons). Thus [illegible] transfer of one [illegible] noble gas con- [illegible] positive charge [illegible] ops a negative charge (chloride ion, Cl^-) bind each other by electrostatic lines of force. The linkage set- [illegible] ionic *bond* while the compoun [illegible] are called *electrovalent com* [illegible] are ionized in solution.



Similarly formation of *magnesium chloride* and *calcium sulphide* can be diagrammatically represented as follows :





Sodium, potassium, magnesium and calcium are elements with low ionization potential. Hence, they tend to lose electrons readily, *i.e.*, they are electropositive elements.

Fluorine, chlorine and sulphur tend to gain electrons due to their higher electron affinity, *i.e.*, these are electronegative elements.

An electrovalent linkage or ionic bond is set up between an electropositive element on one side and an electronegative element on the other side.

(ii) Covalency (By mutual sharing of electrons). [illegible] oxygen and nitrogen molecules are formed by sharing of [illegible] and three electron pairs between their atoms as shown below. [illegible] linkages set up are called single, double or triple bond [illegible]

linkage respectively, generally represented by single, double or

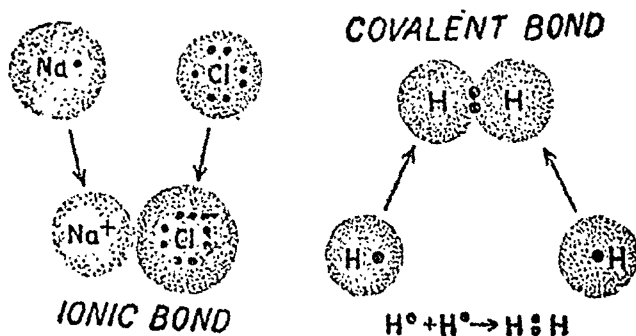
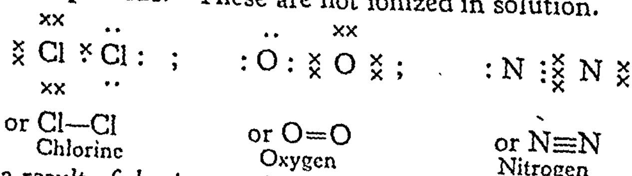


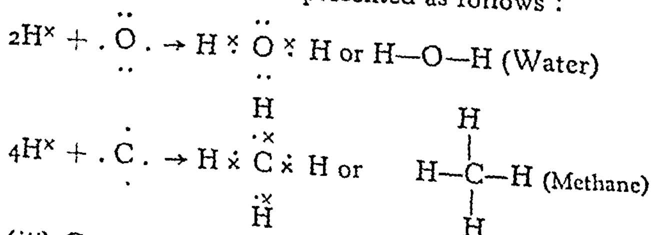
Fig. 10·1—Ionic and covalent bonds.

triple lines. The compounds formed by covalent linkages are called **covalent compounds.** These are not ionized in solution.

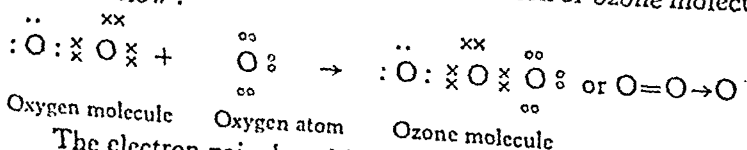


As a result of sharing, each of the atoms has completed its octet and assumed a noble gas configuration.

Similarly electronic structures of water and methane (both covalent compounds) can be represented as follows :



(*iii*) **Co-ordinate valency (By one-sided sharing of electrons).** In a molecule of oxygen octet of each oxygen is complete. If a new oxygen atom deficient by two electrons shares one electron pair belonging to one of the oxygen atoms of the molecule, it will have its octet completed. This is the formation of ozone molecule as shown below :



The electron pair shared is called **lone pair**, the oxygen atom of oxygen molecule is called the **donor** while the new oxygen atom is the **acceptor.** The linkage set-up is called a **co-ordinate linkage** represented by an arrow sign.

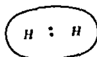
Sulphur dioxide is another example of compounds formed by co-ordinate linkage.



Sulphur dioxide molecule

Electrovalent compounds are generally non-volatile and insoluble in organic solvents. They are good electrical conductors in the fused state or in solution. Covalent compounds are generally volatile and usually soluble in organic solvents. They are non-electrical conductors. Co-ordinated compounds behave very much like covalent compounds but are usually less volatile.

6. Nature of Covalent Bonds.—According to Quantum mechanics, electron is a smeared-out cloud in space and orbital is the space where there is maximum charge intensity. Covalent bonds are set up between different atoms due to the overlapping of the orbitals of their unpaired electrons. For example, formation of hydrogen molecule is represented as given in Fig. 10·2.





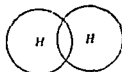
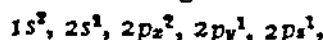
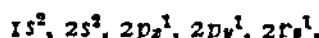


Fig. 10·2—Overlap of electron cloud of hydrogen atoms to form a hydrogen molecule.

Oxygen atom having electronic configuration,

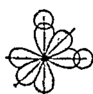

$1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1,$

is divalent due to the presence of two unpaired electrons. Similarly nitrogen atom having electronic configuration,


$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1,$

is trivalent due to the presence of three unpaired electrons.

In the formation of H_2O molecule, two O—H bonds are set up each by overlapping of one p-orbital of oxygen and s-orbital of hydrogen (Fig. 10·3).



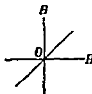
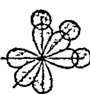


Fig. 10·3—Diagrammatic representation of the directed bonds in the water molecule.



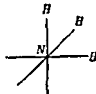


Fig. 10·4—Diagrammatic representation of the directed bonds in the ammonia molecule.

Similarly in the formation of NH_3 molecule, three N—H bonds are set up each by overlapping of one *p*-orbital of nitrogen and *s*-orbital of hydrogen (Fig. 10·4).

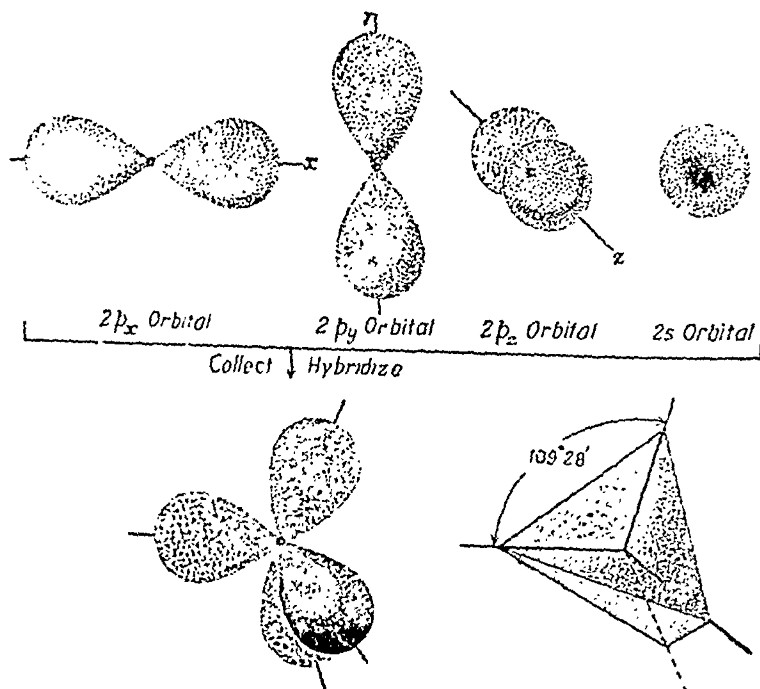
7. **Hybridization.**—Consider the formation of methane. Carbon has the electronic configuration,

$1s^2, 2s^2, 2p_x^1, 2p_y^1.$ (*Ground state*)

There being only two unpaired electrons, carbon should be divalent but carbon is mostly tetravalent. To explain the tetravalency of carbon, it is assumed that one of the 2*s* electrons is excited to $2p_z$ state and the excited carbon atom is

$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1.$ (*Excited state*)

Electron clouds of the four unpaired electrons collect and reshuffle resulting in the formation of four new electron clouds which are identical in all respects. They subtend an angle of 109°—28′ with each other and are directed towards the four corners of a regular tetrahedron. The process is termed **hybridization** *and the new orbitals produced as a result of hybridization are called* **hybridized orbitals.**



Four sp^3 hybrid atomic orbitals with common origin. Tetrahedral hybridization axes of sp^3 hybrid orbitals.

Fig. 10·5—Hybridization of atomic orbitals in a carbon atom (*sp^3 hybridization*).

This accounts for the equivalence of the four valencies of carbon. Since the hybridization has taken place by combining one *s*

and three p orbitals in the above case, it is termed sp^3 (read *sp* three) *hybridization.*

Bonds produced by the overlap of these hybridized orbitals (*hybridized bonds*) are stronger than the original s or p electron bonds. In methane each of the four C—H bonds is formed by the overlap of carbon sp^3 orbital with $1s$ orbital of each hydrogen atom.

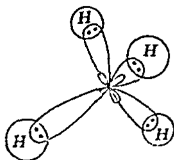
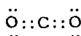
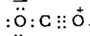
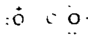


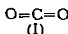
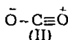
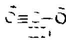
Fig. 10·6—Orbital diagram of methane molecule.

Promotion of the electron from the $2s$ to the $2p$ level requires energy, but the liberation of energy and consequent increase in the stability gained by the formation of four covalent bonds supplies even more energy than is required for promotion of the electron.

8. **Resonance.**—Occasionally no reasonable electronic picture can be drawn for a molecule which could satisfactorily account for its observed properties. For example, the electronic structure of carbon dioxide may be represented by at least three possible electronic arrangements given below

or or

(I) (II)

The calculated heat of formation [illegible] formula is 350 kcal./mole and the O—C [illegible]. However, the observed heat of form[illegible] O—O distance is 2·30Å indicating [illegible] satisfactorily accounts for its observ[illegible] idea that such compounds exist [illegible] tion of two or more electronic [illegible] some contribution to its structure.

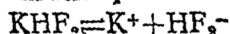
When several structure[illegible] *true structure of a molec*[illegible] *represent it uniquely, the* [illegible] hybrid *and the phenom*[illegible]

The word resona[illegible] that the molecule res[illegible] electron pair jumps ba[illegible] This is totally wr[illegible] structure which ca[illegible] lies in the descrip[illegible]

It is hoped that the following crude analogy will help the readers to grasp the concept of resonance. The mule is a hybrid of the jackass and the mare. When we look at the mule, we do not see a jackass at one glance and mare at another. We see a mule always. In a similar manner a resonance hybrid does not oscillate between its canonical structures. Its properties are fixed and these are the properties of the actual hybrid structure.

9. **Some other Bonds.**—The modern concept of a bond between two atoms is some sort of attraction which keeps the two atoms together. In electrovalent bond it is a strong electrostatic force between the oppositely charged ions. In covalent linkage there is a weaker electrostatic attraction due to mutual interaction of the nuclei and electron clouds of the two atoms. Some other types of bonds we should study are :

(*a*) **Hydrogen Bond.** In some compounds hydrogen atom appears to be bonded to two other atoms simultaneously. For example, the anion HF_2^- in KHF_2



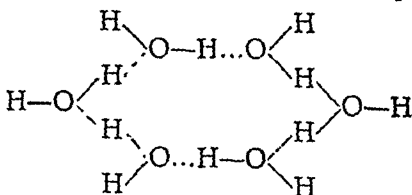
$$KHF_2 \rightleftharpoons K^+ + HF_2^-$$

is believed to have the structure $(FHF)^-$ in which hydrogen acts as a bridge between two fluoride ions. The bond set-up when a proton is shared between two strongly negative atoms is called a hydrogen bond usually indicated by a dotted line. Thus H_2F_2 is represented by the formula



$$H—F...H—F$$

Similarly associated water molecule is represented as :



(*b*) **Van der Waals Attraction.** All molecules exert a weak attraction upon one another due to the mutual interaction of their electrons and the nuclei. There is electrostatic attraction between the nuclei of one molecule and the electrons of the other. This is largely but not completely compensated by the electrostatic repulsion of electrons of one molecule by the electrons of the other and repulsion of the nuclei of one by the nuclei of the other. The resultant weak attraction between the two molecules is termed *van der Waals* attraction.

When the molecules are very close together, the van der Waals attraction becomes significant. Condensation of gases and freezing of liquids on cooling is due to van der Waals attraction. At the boiling point of a liquid the amount of molecular agitation is enough to overcome the forces of van der Waals attraction. The boiling point is, therefore, a measure of these forces.

QUESTIONS

Essay-type Questions

1. What is the Electronic concept of valency? What is the cause of chemical combination? Explain with examples the terms: Electrovalency, Covalent and Co ordinate Valency.
(Chandigarh H.S. 1970; Punjab Pre-Univ. 1971)

2. Write short notes on:
   (a) Hydrogen bond; (b) Van der Waals attraction.
   (c) Difference between Electrovalent and Covalent bonds.
   (d) Valency electrons. *(Delhi H.S. 1973; All India H.S. 1966)*

3. Write a brief note on the electronic structure of atom. Explain, giving illustrations, how chemical combination between elements is explained on the basis of their electronic structure. (Delhi H.S. 1965)

4. (a) Name different types of valency and give two examples of each type.
   (b) Give electronic configuration of (i) Carbon dioxide, (ii) Chloride ion, (iii) Water, (iv) Ammonia, (v) Sodium chloride.
   (All India H.S. 1969, 68, 66)

5. Write short notes on:
   (a) Hybridization; (b) Resonance;
   (c) Overlapping of atomic orbitals and chemical bonding.
   (Chandigarh H.S. 1970)

Test Your Understanding

6. Fill in the blanks in the following
   (i) Electrons present in the outermost shell of an atom are called ....
   (ii) According to the .... valency of an atom is the number of electrons it can ...with other atom or atoms.
   (iii) Sodium is an atom with low........and fluorine is an atom with high ....The bond between them is. ......
   (iv) Condensation of gases and freezing of liquids is on account of....

7. Tick the correct answer from the various alternatives given after each question in the following:
   (a) Two particles have the following compositions:
   12 protons, 12 neutrons, 10 electrons;
   11 protons, 12 neutrons, 10 electrons.
   They would best be described as
   (i) isotopes; (ii) positive ions; (iii) atoms of metals; (iv) anions; (v) atoms of non-metals
   (b) An atom with Z less than 21 and having eight electrons in its outer shell (i) may be inert; (ii) easily loses electrons, (iii) is a metal; (iv) forms ionic compounds; (v) must be inert.
   (c) Match the atomic numbers—4, 14, 8, 15, 19 to each of the following elements:
   (i) a gas of valency 2; (ii) a metal of valency 2;
   (iii) a non-metal of valency 4; (iv) a metal of valency 1;
   (v) a solid non-metal of valency 3.

KEY

6. (i) valency electrons, (ii) electronic theory, lend, borrow or share, (iii) ionization energy, electron affinity, ionic, (iv) hydrogen bonding, (v) Van der Waals attraction.

7. (a)—(ii); (b)—(v); (c)—(i) 8; (ii) 4; (iii) 14; (iv) 19; (v) 15.

Properties of Gases

1. The Gaseous State.—Out of the three states of matter the gaseous state is known for the simplicity and uniformity of its behaviour For example, the following are the characteristic properties of all gases irrespective of their colour, odour or chemical nature :

(i) *Indefinite expansibility.* Gases expand indefinitely and fill any vessel, no matter how large, in which these are placed.

(ii) *Compressibility.* Gases are readily compressible.

(iii) *Diffusion.* They intermix freely with other gases or move into empty space without any difficulty.

(iv) *Homogeneity.* Pure gases or their mixtures are all homogeneous in composition.

(v) *Low density.* Gases possess relatively low density.

(vi) *Gases exert pressure.* A gas exerts pressure on the walls of the container. This pressure increases with the rise of temperature.

These properties of gases are explained on the assumption *that gases are made up of particles (molecules) which are relatively far apart and are in rapid motion. These particles are constantly colliding against the walls of the container and these wall collisions determine the pressure of the gas. With increase of temperature they move still more rapidly.*

2. Boyle's Law.—According to this law, as stated by Robert Boyle in 1662, "*Temperature remaining constant, the volume of the given mass of a gas is inversely proportional to its pressure.*"

This means that if pressure on a gas is doubled, its volume decreases to one-half of the original vloume. Mathematically:

$$V \propto \frac{1}{P}$$

or $$PV = \text{a constant}$$

or $$P_1V_1 = P_2V_2$$

whence $$V_2 = \frac{P_1V_1}{P_2}$$

where V_1 = the original volume,

P_1 = the original pressure,

V_2 = the final volume, and

P_2 = the final pressure.

The pressure of the gas may be stated in any convenient units (generally in terms of mm. of mercury) provided both pressures (original and final) are expressed in the same units.

How does the particle model explain Boyle's law? Consider a certain [illegible] the gas is halved, the number of particles per unit volume is doubled. With twice as many particles per unit volume, the frequency of wall collisions and hence the pressure is doubled.

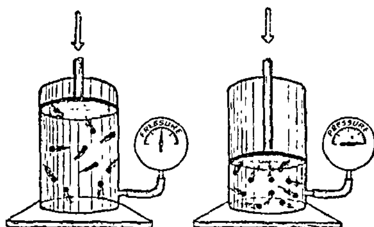


Fig. 11·1—In the particle model of gases, wall collisions determine pressure. Halving the volume, doubles the pressure.

Example 1. *A given mass of gas occupies 112 ml. at a pressure of 740 mm. What volume will it occupy at 760 mm. pressure, temperature remaining constant?*

Here : $V_1=112$ ml. $V_2=?$
$P_1=740$ mm. $P_2=760$ mm.

Now $$V_2=\frac{P_1V_1}{P_2}=\frac{740\times 112}{760}=109 \text{ ml.}$$

3. **Charles Law.**—According to Charles' Law, *pressure remaining constant, the volume of the given mass of a gas is directly proportional to its absolute temperature.*

This means that if absolute temperature of a gas is doubled, its volume will likewise be doubled. Mathematically :

$$V \propto T$$

or $$\frac{V}{T}=\text{a constant}$$

or $$\frac{V_1}{T_1}=\frac{V_2}{T_2}$$

whence $$V_1T_2=V_2T_1$$

or $$V_1=\frac{V_1T_2}{T_1}$$

where

V_1=the original volume,

T_1=the orig. abs. temp.,

V_2=the final volume, and

T_2=the final abs. temp.



Jacques Alexandre Cesar Charles
(1746—1823)
A French physicist ; discovered the law known after his name ; was the first to make a balloon ascend and use hydrogen in balloons.

Absolute temperature=Centigrade temp.=273
or $$A=C+273.$$

Example 2. *A given mass of gas occupies 225 ml. at 15°C. What volume will it occupy if its temperature is raised to 20° at constant pressure ?*

Here $V_1=225$ ml. $V_2=?$
$T_1=15+273=288°$ Abs. $T_2=20+273=293°$ Abs.

Now $$V_2=\frac{V_1T_2}{T_1}=\frac{225\times 293}{288}=228\ 9 \text{ ml.}$$

4. **Gay-Lussac's Law.**—According to this law, *volume remaining constant, the pressure exerted by a given mass of a gas is directly proportional to its absolute temperature. Mathematically :*

$$P \propto T$$

or $$\frac{P}{T}=\text{a constant}$$

Of the three variables controlling the gaseous state, two of the possible pairs have been related keeping the third constant.

Once the Boyle's law $\left(V \propto \frac{1}{P}\right)$ and Charles' law ($V \propto T$) are known, the third ($P \propto T$) follows easily.

... Law, Molecules of ... st the walls of the ... hits and depends ... requency of these collisions.

As the temperature increases the kinetic energy of the molecules increases and the pressure increases. Since kinetic energy of the molecules is directly proportional to the absolute temperature, the pressure must be directly proportional to the absolute temperature.

5. **The Gas Equation.**—The laws of Boyle and Charles can be combined into one equation called the gas equation as follows :

Let the volume of a gas change from V_1 to V_2 when the pressure changes from P_1 to P_2 and temperature changes from T_1 to T_2. To find a relationship between them, let these changes take place in steps :

(*i*) First let the volume change from V_1 to v when the pressure is changed from P_1 to P_2 at constant temperature ($=T_1$). According to Boyle's Law :

$$P_2 v = P_1 V_1$$

or $$v = \frac{P_1 V_1}{P_2} \quad ...(1)$$

(*ii*) Now let the volume change further from v to V_2 when the temperature is changed from T_1 to T_2 at constant pressure ($=P_2$). According to Charle's Law :

$$\frac{v}{T_1} = \frac{V_2}{T_2}$$

or $$v = \frac{V_2 T_1}{T_2} \quad ...(2)$$

Equating the value of v from (1) and (2), we have

$$\frac{P_1 V_1}{P_2} = \frac{V_2 T_1}{T_2}$$

or $$P_1 V_1 T_2 = P_2 V_2 T_1 \quad ...(3)$$

or $$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad ...(4)$$

Equation (3) or (4) is termed Gas equation and is useful in conversion of gas volume from the temperature and pressure to another.

Standard ...
and 760 mm. ...
and pressure ...

Example 3. *100 ml. of nitrogen collected at 27°C and 720 mm. are cooled to −73°C under a pressure of 760 mm. What is the volume occupied by it ?*

$V_1 = 100$ ml. $\qquad V_2 = ?$

$P_1 = 720$ mm. $\qquad P_2 = 760$ mm.

$T_1 = 27 + 273 = 300°$ Abs. $\qquad T_2 = -73 + 273 = 200°$ Abs.

Applying the Gas Equation, $\frac{P_1V_1}{T_2} = \frac{P_2V_2}{T_2}$, we have,

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{720 \times 100 \times 200}{300 \times 700} = 63{\cdot}16 \text{ ml.}$$

6. Dalton's Law of Partial Pressures.—Dalton observed long ago that *if two or more gases which do not react chemically are enclosed in a closed space, the total pressure, P, exerted by the gaseous mixture is the sum of partial pressure, p_1, p_2, p_3, etc., which each one will exert if present alone in that space.* This is known as Dalton's law of partial pressures.

Mathematically : $P = p_1 + p_2 + p_3$.

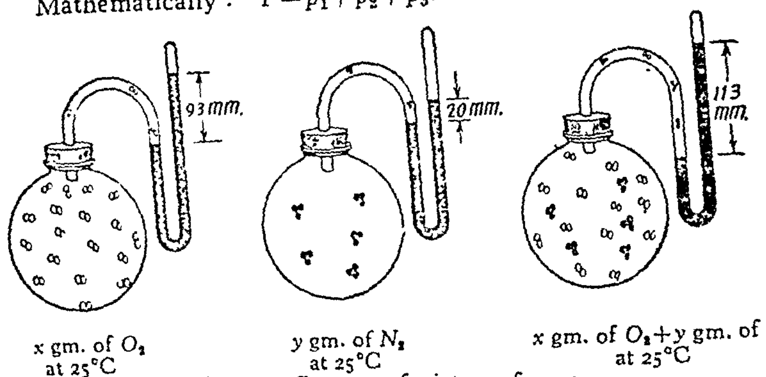


Fig. 11·2—Pressure of mixture of gases.

Example 4. *At constant temperature, 250 ml. of nitrog at 720 mm. pressure and 380 ml. of oxygen under 650 mm. pressu were put in a litre flask. What will be the final pressure of t mixture ?*

(a) *Calculating the partial pressure of nitrogen :*

$V_1 = 250$ ml. $\qquad V_2 = 1000$ ml.

$P_1 = 720$ mm. $\qquad P_2 = ?$

Substituting in the Boyle's law equation, $P_1V_1 = P_2V_2$,

we have $\qquad 720 \times 250 = P_2 \times 1000$

whence $\qquad P_2 = \frac{720 \times 250}{1000} = 180$ mm.

(b) *Calculating the partial pressure of oxygen :*

$V_1 = 380$ ml. $\qquad V_2 = 1000$ ml.

$P_1 = 650$ mm. $\qquad P_2 = ?$

INDISPENSABLE FOR ALL CHEMISTS

$$PV = RT$$

BOYLE'S LAW

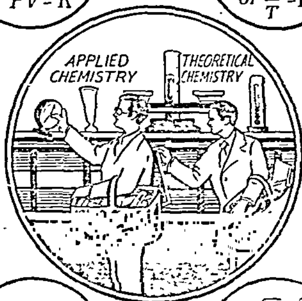
$$V \propto \frac{1}{P}$$

or $PV = K$

CHARLES' LAW

$$V \propto T$$

or $\frac{V}{T} = K$



$$P = p_1 + p_2 + p_3$$

DALTON'S LAW

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Fig 11·3—Gas Laws.

Substituting these values in the Boyle's law equation $P_1V_1 = P_2V_2$, we have

$$650 \times 380 = P_2 \times 1000$$

whence
$$P_2 = \frac{650 \times 380}{1000} = 247 \text{ mm.}$$

(c) *Total pressure of the gaseous mixture according to the Dalton's law of partial pressures is the sum of the partial pressures of the various constituents.*

$\therefore$ Total pressure $= 180 + 247 = 427$ mm.

7. **Utility of Gas Law to a Chemist.**—A chemist is interested in the study of chemical changes. He is required to know the masses of the substances reacting and products obtained. He can directly determine the masses of solids and liquids by weighing but gases cannot be weighed directly. Measurement of the mass of a gas is made possible by these gas laws as follows :

(i) Knowing the pressure P exerted by the moist gas directly and aqueous tension p_1 at that temperature from the tables, pressure p_2 of the dry gas is calculated with the help of Dalton's law of partial pressures

$$p_2 = P - p_1.$$

(ii) Knowing the pressure, volume and temperature of the dry gas, its volume at N.T.P. can be calculated with the help of gas equation which is a combination of Boyle's law and Charles' law

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}.$$

(iii) Knowing the volume at N.T.P. and applying the weight and volume relationship (*22·4 litres of each gas at N.T.P. weigh equal to its gm. mol. wt.*), mass can be easily calculated.

The example given below will make the utility of these laws clear.

Example 5. *Volume of a gas collected over water at 13°C measured 47·8 ml. under 765 mm. pressure. What would be the volume of the dry gas at N.T.P. ?*

[*Aqueous tension at 13°C = 11·2 mm.*]

Here :

$V_1 = 47·8$ ml.	$V_1 = ?$
$P_1 = 765 - 11·2 = 753·8$ mm.	$P_2 = 760$ mm.
$T_1 = 273 + 13 = 286°$Abs.	$T_2 = 273°$ Abs.

Applying the Gas Equation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$, we have

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{753·8 \times 47·8 \times 273}{760 \times 286} = 45·26 \text{ ml.}$$

8. **Gaseous Diffusion.**—When a bottle of some perfume is opened in one corner of a room, its odour is perceptible in all parts

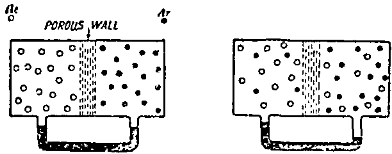


Fig. 11·4 —Helium and argon initially at same temperature and pressure are separated by a porous partition. After some time pressure in the right chamber increases because helium being lighter diffuses more quickly.

of the room even when the intervening air is at rest. This is due to the property of the perfume vapours, in common with other gases, to intermingle freely with the air of the room.

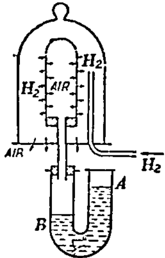


Fig 11·5—Lighter gases diffuse more quickly than heavier ones.

Expt. 1. Invert an empty cylinder (it is full of air) over another full of bromine vapours. In spite of the fact that bromine vapours are six times as heavy as air, these will be seen rising up and make a uniform mixture with air in the upper jar.

Such a spontaneous intermingling of two or more gases is termed diffusion.

Cause of Diffusion. Diffusion is caused by the inherent tendency of a system to lower its free energy by decreasing enthalpy and/or increasing entropy (*see* page 1·26). The intermixing causes increase in randomness or entropy and thus lowers free energy.

The molecules of two gases are relatively far apart and are in rapid motion. These are constantly colliding with each other and against the walls of the container. Their rapid movement helps in intermixing

Lighter gases diffuse more quickly. When two gases are separated by a porous partition, intermingling still occurs though slowly. *Lighter gases diffuse more quickly than heavier ones.* It is illustrated diagrammatically in Fig. 11·4. This can be easily demonstrated in the laboratory.

Expt. 2. Take a porous pot fitted with a cork and a glass tube. The other end of the glass tube is fitted into the neck of a U-tube containing coloured water (Fig 11·5). The porous pot is surrounded by a bell-jar and hydrogen gas is passed into it. Since hydrogen is much lighter than air, it diffuses into the porous pot more rapidly than the air within can diffuse out. This results in the increase of pressure inside the porous pot, which depresses the

level of coloured water in the arm *B* of the U-tube. Coloured water stands higher in limb *A* than in *B*.

Now remove the bell-jar. Hydrogen present inside the porous pot diffuses out more rapidly than the air can pass in. This results in fall of pressure inside the porous pot. The level of coloured water in the U-tube is found to rise in *B* and fall in *A*.

Marsh gas Detector, used by miners, is a practical application of the phenomenon of diffusion. The principle underlying it can be easily demonstrated in the laboratory.

Expt. 3. Fit up the apparatus shown in the diagram (Fig. 11·6). Invert a cylinder full of marsh gas over the porous pot. Marsh gas being lighter than air diffuses in more quickly than air can come out. This results in increase in pressure inside. The mercury column rises in the right limb and makes contact with the wire. Electric circuit is completed and the bell starts ringing. Now remove the marsh gas cylinder. Marsh gas inside the porous pot diffuses out more quickly again than air can diffuse in. This results in fall of pressure inside and the mercury column in the right limb falls. The contact with the copper wire is broken and the bell stops ringing.

In the mine, ringing of the electric bell serves as a warning to the miners about the presence of dangerous marsh gas in the mine.

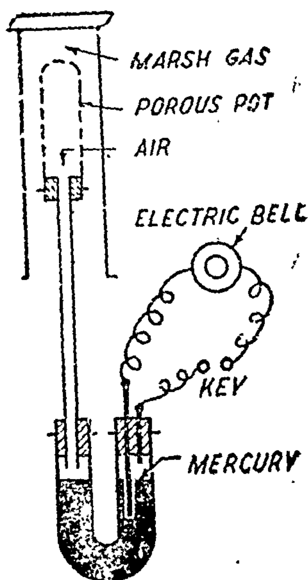


Fig. 11·6—Marsh gas detector

9. **Graham's Law of Diffusion.**—*For any specified temperature and pressure the relative rates of diffusion of gases through a porous partition are inversely proportional to the square roots of their densities.* This is *the Law of Graham* (1822). Mathematically:

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \qquad \ldots(1)$$

As *Molecular weight*$=2\times$*vapour density*, the above law can be written as:

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{2d_2}{2d_1}} = \sqrt{\frac{M_2}{M_1}} \qquad \ldots(2)$$

where r_1, r_2 are the rates of diffusion, d_1, d_2 their densities and M_1, M_2 the molecular weights of two gases respectively.



Thomas Graham (1805–1869) English chemist who enunciated the Law of Gaseous Diffusion.

The time taken for diffusion of a certain volume of a gas is also inversely proportional to its rate of diffusion, *i.e.*,

$$t \propto \frac{1}{r} \quad \text{or} \quad \frac{t_1}{t_2} = \frac{r_2}{r_1} \qquad \ldots(3)$$

∴ From equations (1) and (3) the Graham's Law can also be mathematically stated as follows :

$$\frac{t_1}{t_2}=\sqrt{\frac{d_1}{d_2}}$$

For example, density or molecular weight of oxygen is 16 times that of hydrogen. Hydrogen, therefore, diffuses more rapidly, in fact $\sqrt{16}=4$ times as rapidly as oxygen. Now if 100 ml. of hydrogen diffuse through a porous partition in t seconds, only 25 ml. of oxygen pass through it in the same time.

Similarly, if 100 ml. of hydrogen diffuse through a porous pot in 5 seconds, same volume of oxygen will take 20 seconds to diffuse through the same porous pot.

Effusion is a particular case of diffusion of a gas taking place from a closed space into air through a small aperture.

10. **Utility of Graham's Law to a Chemist.**—Graham's Law finds use in the determination of approximate densities of gases by comparing their rates of effusion. The method, as introduced by Bunsen, can be described as follows :

Apparatus. Bunsen's Effusiometer, the apparatus used for the determination of relative densities of gases, consists of.

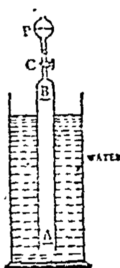


Fig. 11·7—Bunsen's Effusiometer.

(i) A glass tube open at the lower end and provided with a tap C at the upper end.

(ii) A glass bulb attached to a tap C and a thin platinum plate P with a pin hole at its centre, tightly fitting into the bulb.

This is dipped in water or mercury in a trough as shown in Fig. 11·7.

Procedure. The tube is filled with the first gas and the tap is opened. Due to effusion of the gas the water level is rising in the tube. Time t_1 required by the water column to rise from level A to B is noted The experiment is repeated with the second gas and time t_2 noted.

Calculations. t_1 and t_2 are the times taken by equal volumes (say, V c.c.) of two gases to diffuse. Then

$$r_1=V/t_1 \quad \text{and} \quad r_2=V/t_2$$

or

$$\frac{r_1}{r_2}=\frac{t_2}{t_1}$$

Now applying Graham's law, we have

$$\frac{r_1}{r_2}=\frac{t_2}{t_1}=\sqrt{\frac{d_2}{d_1}}$$

Knowing t_1 and t_2, d_1 and d_2 can be compared.

Example 6. *16 ml. of hydrogen were found to diffuse in 30 seconds. What volume of sulphur dioxide would diffuse in the same time under the same conditions ?*

Let v c.c. of sulphur dioxide diffuse in 30 seconds.

r_1 for hydrogen $=16/30$

r_2 for sulphur dioxide $=v/30$

d_1, density of hydrogen (H_2) $=1$

d_2, density of sulphur dioxide (SO_2)$=\dfrac{\text{Mol. wt.}}{2}=\dfrac{64}{2}=32.$

Applying Graham's Law :

$$\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}$$

or $$\frac{16/30}{v/30}=\sqrt{\frac{32}{1}}$$

or $$\frac{16}{v}=\sqrt{\frac{32}{1}}$$

whence $$v=\frac{16}{\sqrt{32}}=\frac{16}{4\sqrt{2}}=2\sqrt{2}\text{ ml.}$$

∴ Volume of sulphur dioxide that will diffuse in 30 seconds (time taken by 16 ml. of hydrogen to diffuse)$=2\sqrt{2}$ ml.

11. **Kinetic Theory of Gases.**—Various gas laws given in this chapter have been obtained by the use of inductive reasoning based on experimental data. The behaviour of a gas under given conditions can be easily predicted with the help of these laws but they do not give us an insight into the nature of the gas. Common properties of different gases are now explained on the assumption that *gases are made up of molecules which are relatively far apart and are in rapid motion.* This kinetic hypothesis had been suggested in 1678 by *Robert Hooke* and adopted in 1738 by *Daniel Bernoulli.* It was developed and worked out by German physicists *Kronig* and *Clausius* in 1856 and 1857 and then by Scottish physicist *Clark Maxwell* in 1860 into what is at present known as the kinetic theory of gases.

Postulates of the Kinetic Theory of Gases. According to this theory :

(*i*) *Gases consist of tiny molecules, which are so small and so far apart on the average that the actual volume of the molecules is negligible compared to the empty space between them.*

(*ii*) *The molecules are moving very fast in straight lines at random and straight line motion colliding with each other and with the walls of the container. Pressure is exerted by gases because molecules collide with the walls of the container.*

(iii) The molecules are perfectly elastic and in each collision there is no net loss of kinetic energy, although there may be transfer of energy between the partners in the collision.

(iv) There are no forces of attraction between the molecules which are completely independent of each other.

(v) The effect of gravity on the motion of the molecules is negligible in comparison to the effect of continued collisions between them.

(vi) At a particular instant different molecules in a sample have different speeds and hence different kinetic energies. However, the average kinetic energy of the molecules is assumed to be directly proportional to the absolute temperature.

Volume, Pressure and Temperature of a gas in the light of above postulates :

(i) **Volume.** The volume of a gas is mostly empty space in which billions of tiny molecules are in rapid motion.

(ii) **Pressure.** The pressure of a gas is because its molecules are colliding against the walls of the container.

(iii) **Temperature.** The temperature of a gas is a measure of the average kinetic energy of its molecules. Greater the kinetic energy, higher will be the temperature.

12. Validity of the Postulates of the Kinetic Theory of Gases.

(i) Extreme compressibility of a gas is a proof of the large empty space in it [*Postulate (i)*]. It has been calculated that 99·96% of the total volume of oxygen at N.T.P. is empty space.

(ii) Dust particles in air are found to be in constant irregular zig-zag motion termed *Brownian motion*. This implies the very fast straight line motion of the molecules [*Postulate (ii)*].

(iii) Rapid motion of so many molecules must involve frequent collisions between them. These collisions must be elastic [*Postulate (iii)*] as otherwise there will be constant loss of kinetic energy and ultimately the molecules must come to rest (something which does not happen).

(iv) In a compressed gas the molecules are very close and inter-molecular attraction is the highest. This attraction must be negligible [*Postulate (iv)* as even a highly compressed gas expands freely and fills the whole available space.

(v) Diffusion is an inherent property of gases. Even a heavier gas rises up to intermix with a lighter gas. This suggests that the effect of gravity is negligible in comparison to the effect of continued collision between them [*Postulate (v)*].

(vi) On heating the temperature of gas rises. Heat energy supplied increases the speed of the molecules and their average kinetic energy increases resulting in rise of temperature [*Postulate*

QUESTIONS AND PROBLEMS

Essay-type Questions and Problems

1. State gas laws associated with the names of Boyle, Charles, Dalton, Avogadro and Graham. *(Delhi H.S. 1973, 63 ; Punjab H.S. 1962, 61)*

An unknown gas diffuses four times as quickly as oxygen. Calculate molecular weight of the gas. *(Punjab Pre-University 1964)*

2. Define the various gas laws with which you are familiar. How can the gas equation be derived from them ?

3. What is Graham's Law of Diffusion ? Describe an experiment to show that hydrogen diffuses more rapidly than air.
(Delhi H.S. 1964 ; Chandigrah 1970)

4. How will you explain the following on the basis of the particle model of gases :
(a) Difference between solid, liquid and gaseous states, and
(b) Diffusion of gases ? *(Chandigarh H.S. 1970)*

5. What do you understand by the volume, pressure and temperature of the gas on the basis of the kinetic theory of gases ?
(Punjab Pre-Medical/Pre-Engg./B.Sc. I Year 1969)

Charles' Law

6. (a) Density of air is 0·001293 gm./ml. What is its vapour density ?
(b) At what temperature centigrade will the volume of a gas at 0°C double itself, pressure remaining constant ? *(U.P. Board Inter. 1967)*

[Hint. Vapour density of air is its relative density as compared to that of hydrogen, *i.e.*,

$$\text{Vapour density of air} = \frac{\text{density of air}}{\text{density of } H_2}.]$$

7. A certain mass of gas occupies 38 ml. at 27°C and 750 mm. pressure. At what temperature will it exert a pressure of 720 mm.
(Bombay First Year Science 1963)

Gas Equation

8. A certain mass of dry hydrogen occupies 50 ml. at 27°C and under 750 mm. pressure. What volume will it occupy at 17°C and under 760 mm. pressure ? *(Bombay First Year Science 1962)*

9. If 20 litres of oxygen is collected over water at 27°C and 756·7 mm. pressure, what would be the volume of dry oxygen at N.T.P. ? (Aqueous tension at 27°C is 26·7 mm.) *(Delhi H.S. 1973)*

10. Volume of moist oxygen at 23°C and 800 mm. pressure is 100 ml. Calculate the volume of dry oxygen at N.T.P. (*Aqueous tension at 23°C is* 21 mm.) *(Delhi H.S. 1965)*

11. An air bubble is blown into a eudiometer tube 50 cm. long and filled with mercury. If the volume of the air bubble before introduction was 0·5 ml., find its volume on reaching the top of mercury in the eudiometer [Pressure of air=750 mm. Hg ; Ignore the change in level of mercury on introducing air bubble.]

Dalton's Laws of Partial Pressures

12. At constant temperature, 250 ml. nitrogen at 720 mm. pressure and 380 ml. oxygen under 650 mm. pressure were put in a one-litre flask. What will be the final pressure of the mixture ?

Miscellaneous

13. A cylinder of 1 litre capacity is to be filled with hydrogen at 8 atmospheres pressure at 27°C. What will be the density of hydrogen in the cylinder ? What will be the volume of this hydrogen at N.T.P. ? (*At. wt. of* H=1.) *(I.I.T. Admission Test 196*

14. Core of the sun is made up of gases with average atomic weight= Their density and pressure are 1·3 gm/ml. and $1{\cdot}12 \times 10^9$ atm. respectively. Calculate the temperature of the sun. *(I.I.T. Admission Test 196*

Relative Density

15. The speed of diffusion of carbon dioxide and ozone were found to be as 0·29 is to 0·274. The relative density of CO_2 is 22 when $H_2=1$. What is the relative density of ozone? *(Delhi H.S. 1964)*

Molecular Weight

16. 57 ml. of hydrogen takes the same time for diffusion through a porous vessel as 10 ml. of another gas G. Calculate the molecular weight of G. *(Punjab Pre-University 1969)*

[illegible]

(Madhya Pradesh Inter. 1964)

[Hint: Calculate the density of ozonised oxygen. Let it be a. The gas is a mixture of 1 part (20%) of ozone (density=x) and 4 parts (80%) of oxygen (density=16).

$\therefore$ Density of mixture $=\dfrac{x+4\times 16}{5}=a$ *(calculated already)*

From here calculate the value of x.]

[illegible]

Time Required for Diffusion

19. If 150 ml. of oxygen take 25 seconds to diffuse through a porous lid, how long will 200 ml. of carbon dioxide take to diffuse under the same conditions? Molecular weights of oxygen and carbon dioxide are 32 and 44 respetcively. *(Bihar H.S. 1962)*

20. How long will it take 750 ml. of chlorine to diffuse through a porous partition if 300 ml. of oxygen diffuse through the same partition in 50 seconds? *(Rajasthan Pre-Uni. 1966)*

Test Your Understanding

21. (a) State how the particle model of gases can explain the following:

(i) Gases are miscible freely.

(ii) The pressure exerted by a gas increases as its temperature is increased.

(b) Given the volume of a definite amount of a gas at a given temperature and pressure, what change will occur in each of the following cases:

(i) The temperature is kept constant but the pressure is reduced to one-fourth of the original pressure.

(ii) The pressure is kept constant but the absolute temperature is raised three times its original value.

(iii) The volume is kept constant but the absolute temperature is lowered to one-half of its original value.

(iv) The pressure is halved and the absolute temperature is doubled. *(Punjab Pre-University 1971)*

ANSWERS

1. 2. 6. (a) 14 37; (b) 273°C.

7. 15°C. 8. 47·7 ml. 9. 17 48 litres.

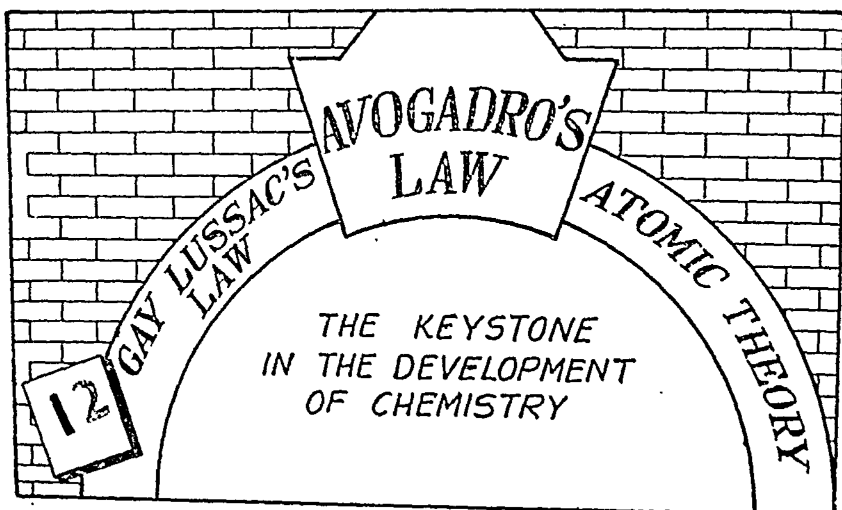
10. 54 52. 11. 1·5 ml. 12. 427 mm.

13. Density=6 667 gm./litre ; Volume=74 62 litres.

14. $2\cdot 1\times 10^{17}$A. 15. 24·63. 16. 64 98 17. 22·80.

18. 16. 19. 39 08 seconds. 20. 186 2 seconds.

21. (a) (i) The volume increases 4 times.
(ii) The volume increases 3 times
(iii) The pressure becomes one-half.
(iv) The volume remains unchanged.



Avogadro's Law

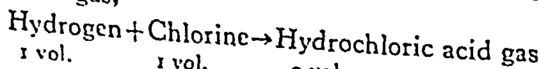
1. **Berzelius Hypothesis.**—The Swedish chemist, Berzelius was trying to correlate Gay Lussac's Law and Dalton's atomic theory. He argued that *Elements combine in a simple ratio by atoms (Dalton's atomic theory) while Gases combine in a simple ratio by volumes (Gay Lussac's law).*

Combining these two facts it follows that in the case of gaseous elements there is (*i*) a simple ratio by *atoms* as well as (*ii*) a simple ratio by *volumes*.

Consequently in the case of gases, there must be some relationship between the volume of a gas and the number of atoms it contains. He stated a relationship known after his name, Berzelius hypothesis, as follows :

Equal volumes of all gases under similar conditions of temperature and pressure contains equal number of atoms.

The term 'atom' included compound atoms of Dalton as well. The hypothesis when applied to certain gas reactions was found to be in direct conflict with Dalton's atomic theory. For example, in the case of combination of hydrogen and chlorine to give hydrochloric acid gas,



Hydrogen +	Chlorine →	Hydrochloric acid gas
1 vol.	1 vol.	2 vol.
n atoms	n atoms	2 compd. atoms
½ atom	½ atom	1 compd. atom

one volume of hydrogen is found to combine with one volume of chlorine to give two volumes of hydrochloric acid gas. Applying Brezelius hypothesis these will contain *n*, *n* and 2*n* atoms respectively.

This means that n a... atoms of chlorine to give 2n co... Or one compound atom of ... 1 ... m of hydrogen and ½ atom of chlorine. This involves fractions of atoms which are indivisible according to Dalton's atomic theory. The hypothesis was, therefore, considered untenable and rejected.

2. Avogadro's Law.—Another Italian chemist, Avogadro, in 1811, distinguished between two kinds of ultimate particles of matter, an atom and a molecule. According to him,

An atom is the smallest particle of an element which can take part in a chemical reaction. It may or may not be capable of free existence.

... matter (element or com-
... matter which can exist free in a gas is the molecule and not the atom, the volume of a gas should, therefore, be related to the number of molecules present in it, not the atoms. He stated the relationship, called after his name *Avogadro's hypothesis*, as follows :

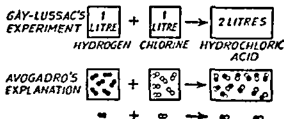


Fig. 12 1

Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.

The hypothesis was scoffed at by his contemporaries who considered it to be of no importance. After some time when further experiments indicated rather strongly in favour of the hypothesis, it was named Avogadro's theory. Now we no longer term it as Avogadro's hypothesis or his theory but speak of it as Avogadro's law.


Amedeo Avogadro
(1776—1856)
An Italian physicist who is famous as an author of the law which bears his name.
FIC—4-72—8

The reaction between hydrogen and chlorine can be explained in terms of Avogadro's law as follows :

Hydrogen +	Chlorine →	Hydrochloric acid gas
1 vol.	1 vol	2 vol.
n mol	n mol.	2n mol.
½ mol.	½ mol.	1 mol

It follows that 1 molecule of hydrochloric acid is made up of ½ molecule each of hydrogen and chlorine. Now ½ molecule is possible and may be made up of one or more atoms. Thus the result is no way in clash with Dalton's atomic theory.

3. **Importance of Avogadro's Law.**—Avogadro's law has gone a long way in the development of chemistry. Its importance or usefulness lies in its numerous applications as given below :

(*i*) **Modification of Atomic Theory.** By making the distinction between an atom and a molecule clear, it has modified Dalton's atomic theory and thus placed it on a firm footing.*

(*ii*) **Interpretation of Gay Lussac's Law.** In the reaction between two gases X and Y, let a molecules of X react with b molecules of Y where a and b are simple whole numbers. According to Avogadro's hypothesis equal volumes of the two gases X and Y (say, 1 c.c.) contain equal number of molecules (say $=N$) under similar conditions of temperature and pressure.

∴ Volumes X and Y which react are a/N c.c. and b/N c.c. respectively. These bear a simple ratio $a : b$ to each other, *i.e.*, there exists a simple ratio between the volumes of gases which react with each other. This is *Gay Lussac's Law of Gaseous Volumes.*

(*iii*) **Deduction of Atomicity of elementary gases.** *Atomicity of an element is the number of atoms contained in its molecules.* In the reaction given above between hydrogen and chlorine to give hydrochloric acid we have seen that one molecule of hydrochloric acid contains half a molecule of hydrogen.

The number of replaceable hydrogen atoms present in one molecule of the acid is called its basicity. It is equal to the number of series of salts the acid gives. For example, sulphuric acid gives rise to two series of salts, sulphates and bisulphates, it is dibasic. Similarly, phosphoric acid gives rise to three series of salts, it is tribasic. Now hydrochloric acid gives rise to only one series of salts, *viz.*, chlorides. It is, therefore, monobasic, *i.e.*, it contains only one atom of hydrogen. But we have found above that it contains ½ molecule of hydrogen.

∴ ½ molecule of hydrogen $=1$ atom

or 1 ,, ,, ,, $=2$ atoms

i.e., molecule of hydrogen is diatomic or its atomicity is two.

(*iv*) **Derivation of the relationship :**

$$\text{Mol. Wt.} = 2 \times \text{V.D.}$$

Vapour density of a gas is a number telling us as to how many times it is heavier as compared with hydrogen. It is the ratio between the weights of equal volumes of the gas and hydrogen under similar conditions of temperature and pressure.

Molecular weight of gas is also a number telling us as to how many times its molecule is heavier as compared with an atom of hydrogen.

* The molecular hypothesis (modified atomic theory) is given on page 1·67.

Mathematically :

$$V.D. = \frac{\text{Wt. of a certain vol. of gas or vapour}}{\text{Wt. of same vol. of hydrogen at same temp. and pressure}}$$

Applying Avogadro's hypothesis, we get

$$V.D. = \frac{\text{Wt. of } n \text{ mol. of the gas or vapour}}{\text{Wt. of } n \text{ mol. of hydrogen}}$$

Dividing the numerator and the denominator both by n, we have

$$V.D. = \frac{\text{Wt. of 1 mol. of the gas or vapour}}{\text{Wt. of 1 mol. of hydrogen}} \quad ...(i)$$

From definition of molecular weight, we know

$$\text{Mol. Wt.} = \frac{\text{Wt. of 1 mol. of the gas or vapour}}{\text{Wt. of 1 atom of hydrogen}} \quad ...(ii)$$

Dividing (ii) by (i)

$$\frac{\text{Mol. Wt.}}{\text{V.D.}} = \frac{\text{Wt. of 1 mol. of hydrogen}}{\text{Wt. of 1 atom of hydrogen}} = 2$$

[∵ Molecule of hydrogen is diatomic.]

or $\text{Mol. Wt.} = 2 \times \text{V.D.}$

(v) **In finding Weight-Volume relationship of gases.** Avogadro's law is used in deducing a weight-volume relationship for gases as given below :

Let the weight of 1 atom of hydrogen be w gm.

Then

Weight of 1 molecule of hydrogen $= 2w$ gm.

" " " nitrogen $= 28w$ gm.

" " " oxygen $= 32w$ gm.

[∵ Mol. wts. of hydrogen, nitrogen and oxygen are 2, 28 and 32 respectively, *i.e.*, their molecules are 2, 28 and 32 times as heavy as an atom of hydrogen ($= w$ gm. here) respectively].

Weight of the substance in grams numerically equal to its ... ight or gram mole or ... hydrogen, nitrogen ... ectively

Knowing the weight of one molecule of the gas, we can find the number of molecules present in a certain weight of the gas by dividing total weight of the gas by weight of one molecule. Thus

No. of mol. of hydrogen in one gm. mol. wt. of it $= \frac{2}{2w} = \frac{1}{w}$

" " nitrogen " " " " $= \frac{28}{28w} = \frac{1}{w}$

" " oxygen " " " " $= \frac{32}{32w} = \frac{1}{w}$

This shows that one gm. mol. wt. of each gas contains the same number of molecules ($1/w$). *Equal number of molecules as they*

contain, these will occupy equal volumes. (*Converse of Avogadro's law : Equal number of molecules of all gases occupy equal volumes under similar conditions of temperature and pressure.*)

Thus 1 gm. mol. wt. of every gas will occupy a certain definite volume. This volume occupied by 1 gm. mol. wt. of any gas is called **Gram-molecular volume** and has been experimentally found to be 22·4 litres at N.T.P. *Thus 22·4 litres of any gas at N.T.P. weigh equal to its one gram mol. wt.*—A weight-volume relationship between gases.

(*vi*) **In Gas Analysis.** All eudiometric calculations are based on Avogadro's law. Thus it finds use in determining the composition of gas mixtures and the determination of the formulae of gases from their combustion or similar data. For example, it has been experimentally found that two volumes of ozone on decomposition yield three volumes of oxygen.

Ozone	→	O_2
2 vol.		3 vol.
$2n$ mol.		$3n$ mol.
1 mol.		3/2 mol. = 3 atoms.

According to Avogadro's law, if two vol. of ozone contain $2n$ mol. three vol. of oxygen will contain $3n$ mol. In other words, $2n$ mol. of ozone yield $3n$ mol. of oxygen. Or, 1 mol. of ozone gives 3/2 mol. (= 3 atoms) of oxygen, *i.e.*, the molecule of ozone is made up of 3 atoms of oxygen.

∴ Formula of ozone is O_3.

4. **Avogadro's Number, N.**—The number of molecules present in one gram-molecular weight of any gas is the same (*as* proved above). This number, N is called Avogadro's number or Avogadro's constant. Its value as determined by different methods has been found to be $6·02 \times 10^{23}$.

5. **The Mole Concept.**—We have seen above that one gram-molecular weight of any gas contains the same number (= $6·02 \times 10^{23}$) of molecules. This is true of one gram molecular weight of all substances, gases, liquids or solids. In practice, it is inconvenient to deal with such a large number of individual particles. A bigger unit is, therefore, used for the purpose. This bigger unit is termed the 'mole'. The mole represents :

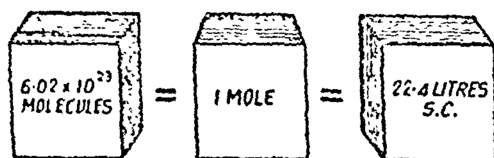


Fig. 12·2.

(*a*) One gram formula weight of a substance, *e.g.*, one mole of sodium chloride (NaCl, formula wt. = 58·5) represents 58·5 g. of sodium chloride.

Note. For more examples about use of Avogadro's Law in Gas Analysis refer to composition of hydrochloric acid, hydrogen sulphide, sulphur dioxide, ammonia, etc. in Non-metals and Eudiometry—Chapter 17.

(*b*) $6·02 \times 10^{23}$ (Avogadro's number) particles of the given substance.

It must be clearly understood that the mole represents only a certain number ($=6·02 \times 10^{23}$) of particles. Thus we may have a mole of marbles, a mole of potatoes, a mole of ions or a mole of electrons. In each case we are talking about $6·02 \times 10^{23}$ particles.

Thus one mole of water (H_2O, formula weight$=18$) represents 18 g. of water or $6·02 \times 10^{23}$ molecules of water. It contains one mole of oxygen atoms and two moles of hydrogen atoms.

We can use mole concept in explaining the terms gram atomic weight and gram molecular weight.

(*i*) Gram atomic weight of an element (its weight in grams numerically equal to its atomic weight) is the weight of one mole ($=6·02 \times 10^{23}$) of atoms of that element.

(*ii*) Gram-molecular weight of a substance (its weight in grams numerically equal to its molecular weight) is the weight of one mole ($=6·02 \times 10^{23}$) of its molecules.

Thus 12 g. of carbon, 1 g. of hydrogen, 14 g. of nitrogen,

acid (H_2SO_4) contains 2 moles of hydrogen atoms, one mole of sulphur atoms and four moles of oxygen atoms.

QUESTIONS AND PROBLEMS

Essay-type Questions

1. Enunciate Gay Lussac's law of gaseous volumes and illustrate it by giving suitable examples. What important derivatives have been made on the basis of this law and how? (*Punjab Pre-Univ. 1963; Nagpur 1970*)

2. State Avogadro's hypothesis. Discuss how Gay Lussac's law of combining volumes and Dalton's atomic theory led Avogadro to put forward the hypothesis. Explain how the gram-molecular volume of a gaseous substance at N.T.P. is 22,400 c.c. (*Kashmir Pre-Univ. 1961*)

3. State Avogadro's hypothesis and discuss fully its importance in chemistry. (*Punjab Pre-Univ. 1966, Delhi H.S. 1967, All India H.S. 1968; Madhya Pradesh Inter. 1964*)

4. State and explain Avogadro's hypothesis. Using Avogadro's hypothesis, deduce that—

(*a*) Gram molecular volume of a gas at N.T.P. is 22,400 c.c.

(*b*) Chlorine molecule is diatomic.

(*c*) Molecular weight of a gaseous compound $=2\times$its relative vapour density. (*Nagpur Pre-Univ. 1971, Punjab Pre-Univ. 1969, Bombay 1963*)

5. State the law which describes the relationship between equal volumes of gases and the number of molecules in them. (*Punjab Pre-Univ. 1971*)

6. State Avogadro's law and explain its importance in determining molecular weights. Illustrate your answer by examples. (*Delhi Pre-Medical 1964*)

est Your Understanding

7. Calculate the volume occupied by :

(a) 8 gm. of oxygen ; (b) 1·5 mole of nitrogen ; and

(c) 0·2 mole of carbon dioxide.

8. You are given 0·64 gram of oxygen and 0·42 gram of nitrogen in two ars. Calculate for each :

(a) Volume at N.T.P. ; (b) Number of moles ; and

(c) Number of molecules.

9. Given that Avogadro's number $=6{\cdot}024\times10^{23}$, calculate the weight of an oxygen molecule in grams. What is the effect of pressure and temperature on this weight ? (*Punjab Pre-Univ. 1970, 68*)

10. Criticise the following statement giving reasons :

If 1·12 litres of O_2 contain 3×10^{22} molecules at N.T.P., 0·56 litre of SO_2 will also contain 3×10^{22} molecules. (*Delhi H.S. 1969*)

11. (a) Which of the following weighs most :

(i) 50 g. of iron. (ii) 5 gram-atoms of nitrogen. (iii) 0·1 gram-atom of silver. (iv) 1×10^{23} atoms of carbon.

(b) How many atoms and how many gram-atoms are there in ten grams of calcium ? (*Punjab Pre-Univ. 1969*)

12. (a) Explain clearly the terms 'Mole' and 'Avogadro's number'. Define atomic weight and molecular weight on the basis of mole concept and given one example of each.

(b) What number of molecules of carbon dioxide will weigh 4 grams ? How will you express this weight in moles ?

(c) Calculate the number of molecules of oxygen and nitrogen respectively in a gas jar having a capacity of 2·8 litres at N.T.P.

(d) Find the number of molecules contained in a drop of water weighing 0·04 gm. (*Guru Nank Pre-Univ. 1971*)

KEY

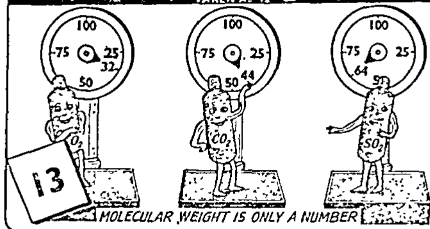
7. (a) 5·6 litres at N.T.P. (b) 33·6 litres at N.T.P.
(c) 4·48 litres at N.T.P.

8. (a) $O_2=448$ c.c. ; $N_2=336$ c.c.
(b) $O_2=0{\cdot}02$ mole ; $N_2=0{\cdot}015$ mole.
(c) $O_2=1{\cdot}204\times10^{22}$; $N_2=9{\cdot}03\times10^{21}$.

9. $5{\cdot}317\times10^{-23}$ gm. ; None.

11. (a)—(ii). (b) $1{\cdot}505\times10^{23}$ atoms ; 0·25 gram-atoms.

12. (b) $1{\cdot}505\times10^{23}$: 0·25 mole.
(c) $7{\cdot}52\times10^{22}$ molecules for both.
(d) $1{\cdot}34\times10^{21}$.



Molecular Weights

1. **What is Molecular Weight ?**—Matter is made up of molecules and molecules are made up of atoms. Atoms and molecules are so small particles that their weights are inconveniently small when expressed in terms of grams. To overcome this difficulty the weight of one-twelfth of a carbon atom is selected as a unit of weight for the purpose and is termed atomic mass unit (amu).

The relative weight of a molecule as compared with the weight of a carbon atom (C^{12} isotope) taken as 12 amu, is called its molecular weight. It does not tell us at all how much a molecule actually weighs. It is, thus, defined as follows :

Molecular weight of a substance is the relative weight of its molecule as compared with the weight of an atom of carbon (C^{12} isotope) *taken as 12 amu.*

It is only a number. By saying that molecular weight of sulphur dioxide is 64, we mean that a molecule of sulphur dioxide is 64 times as heavy as one-twelfth of a carbon atom.

It is also the sum of atomic weights of all the atoms of the molecule. For example,

Mol. wt. of sodium chloride, NaCl = At. wt. of Na + At. wt. of Cl

$= 23 + 35.5 = 58.5$.

2. **Gram-Molecular Weight.**—Weight of the substance in grams numerically equal to its molecular weight is termed its *gram-molecular weight or gram-molecule* (*G.M.W.*).

For example, mol. wt. of oxygen is 32 (it is a number only). Its gram-molecular weight will be 32 grams (it is a weight). Similarly gram-molecular weights of hydrogen, nitrogen, carbon dioxide and sulphur dioxide are 2 gm., 28 gm., 44 gm., and 64 gm., respectively.

3. **Molecular Weights of Gases.**—Molecular weights of gases like nitrogen and oxygen are determined by the following methods :

(*a*) **Gram-Molecular Volume Method.** One gram molecule of each gas occupies 22·4 litres at *N.T.P.* This volume is called gram-molecular volume (*G.M.V.*).

Knowing the weight of a given volume of a gas under given conditions of temperature and pressure, we can calculate the weight of 22·4 litres of the gas at *N.T.P.* This gives the gram-molecular weight of the gas.

Example 1. *2·83 gm. of a gas occupy 3·895 litres at 20°C and 780 mm. pressure. Calculate its molecular weight.*

Calculating the volume of the gas at N.T.P.

$V_1=3{\cdot}895$ litres	$V_2=?$
$P_1=780$ mm.	$P_2=760$ mm.
$T_1=20+273=293°$ Abs.	$T_2=273°$ Abs.

$$V_2=\frac{P_1V_1T_2}{T_1P_2}=\frac{780\times3{\cdot}895\times273}{293\times760}=3{\cdot}725 \text{ litres.}$$

Now Wt. of 3·725 litres of the gas at *N.T.P.*$=2{\cdot}83$ gm. (*Given*)

∴ Wt. of 22·4 ,, ,, ,, or

$$\text{Gram molecular weight of the gas}=\frac{2{\cdot}83}{3{\cdot}725}\times22{\cdot}4=17{\cdot}02 \text{ gm.}$$

whence Molecular Weight$=17{\cdot}02$

(*b*) **Regnault's Vapour Density Method.** *Vapour density of a substance is the ratio of the weight of a certain volume of its vapour and the weight of the same volume of hydrogen under similar conditions of temperature and pressure.* It is only a number denoting how many times a certain gas is heavier than hydrogen. For example, *V.D.* of nitrogen$=14$, means that nitrogen is 14 times as heavy as hydrogen.

The density of gas can be determined by weighing an exhausted globe and reweighing the same after filling it with the gas.

This gives the weight of the gas (=w gm., say) under atmospheric conditions of temperature and pressure.

To eliminate the effect of the buoyancy of air depending upon its temperature, pressure and degree of moisture, Regnault in 1845 made use of a compensating globe. The exhausted globe A is counter-poised against another globe B of nearly the same weight and volume, suspended from the right-hand pan. Thus the two globes are equally affected by any variations in the atmospheric conditions.

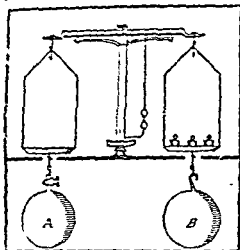


Fig. 13·1—Regnault's Apparatus.

The volume of the globe A is found out by weighing the globe after filling it with water.

Calculations. The volume of the gas is reduced to N.T.P. (=v ml., say). Knowing the weight of v ml. of the gas as w gm., we calculate the weight of 22,400 ml. of it

$$=\frac{w}{v}\times 22{,}400 \text{ gm.} = M \text{ gm.}$$

This gives mol. wt. of the gas as M. Another method for the same is :

$$V.D. = \frac{\text{Wt. of } v \text{ ml. of the gas } N.T.P.}{\text{Wt. of } v \text{ ml. of hydrogen at } N.T.P.}$$

$$= \frac{w}{v \times 0.00009} = x \text{ (say)}$$

Further Mol. wt. $= 2 \times$ V.D. $= 2x$.

(c) Effusion Method. According to Graham's law for any specified temperature and pressure the rates of effusion of gases are inversely proportional to the square roots of their densities or molecular weights. Or, times taken for effusion of equal volumes of two gases are directly proportional to their molecular weights.

Mathematically :

$$\frac{t_1}{t_2} = \sqrt{\frac{M_1}{M_2}}$$

where t_1 and t_2 are times taken for effusion of equal volumes of two gases. These are experimentally determined with the help of the Bunsen's effusiometer (see page 1·107). Knowing one of the molecular weights (M_1 or M_2), the other can

Example 2. *The speeds of diffusion of carbon dioxide and of ozone were found to be 0·58 : 0·542 ; find the molecluar weight of ozone if that of carbon dioxide is known.*

r_1 for carbon dioxide	$=0·58$
r_2 ,, ozone	$=0·542$
M_1 ,, carbon dioxide (CO_2)	$=12+32=44$
M_2 ,, ozone	$=?$

Applying Graham's law :

$$\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}$$

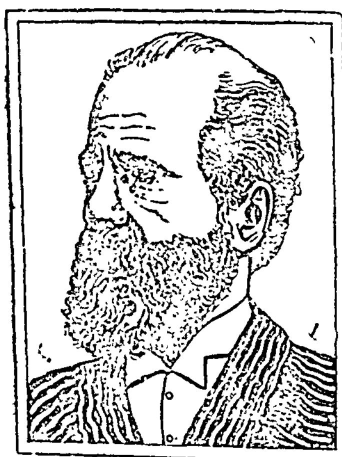
we have

$$\frac{0·58}{0·542}=\sqrt{\frac{M_2}{44}}$$

or

$$\left(\frac{0·58}{0·542}\right)^2=\frac{M_2}{44}$$

whence $M_2=\frac{0·58\times0·58\times44}{0·542\times0·542}=50·39.$



Victor Meyer
(1865–97)
German chemist known for the method known after his name for the determination of molecular weights of volatile substances.

4. Molecular Weights of Volatile Substances.—Molecular weights of volatile liquids and solids can be easily determined by coverting a known weight (say, w gm.) of the substance into vapour. The volume of vapour obtained is measured under atmospheric conditions and then reduced to *N.T.P.* (say$=v$ ml.). Therefore, the weight of 22,400 ml. of the vapour is calculated. This gives the molecular weight. Different methods employed are :

(a) Victor Meyer's Method.

Apparatus Used. Victor Meyer's apparatus used for determining the molecular weight of a volatile substance is shown in Fig. 13·2. It consists of an inner Victor Meyer' tube, *A*, provided with funnel, *F*, at the top, a bulb at the bottom and side tube, S, near the upper end. The top is fitted with a rubber stopper while the lower end is surrounded by a jacket, *J*, containing a liquid of b. p. about 20°C higher than the volatilization temperature of the volatile substance. The bottom of the bulb inside is covered with glass wool or asbestos fibre. The side tube is dipping under water in a trough.

Procedure. The experiment is carried out as follows :

(i) Boil the liquid in the outer jacket when the side tube is dipping under water till no more air bubbles are evolved. This shows that temperature inside the tube is uniform.

(ii) Invert a graduated tube, G, filled with water over bee-hive shelf.

(iii) Weigh out accurately some volatile substance in a Hofmann's bottle, *H*, with a tiny stopper.

(iv) Remove the stopper from *F* for a second, slip in the tiny bottle and replace the stopper immediately. As soon as it reaches the bottom, the volatile substance vaporizes and blows off the tiny stopper. The shape of the tube is such that the vapour pushes an equal volume of air into the graduated tube.

(v) After careful levelling, note down the volume, temperature and pressure of the air collected. For levelling, the graduated tube, partly filled with the air collected, is lowered into a tall jar containing water till the inside level is the same as the outside level (Fig. 13·3). The volume thus noted is the volume of air at atmospheric pressure.

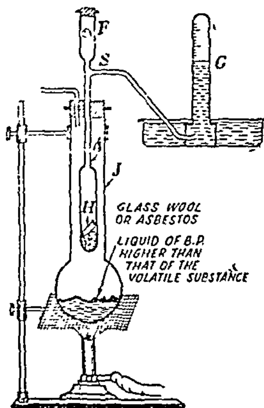


Fig. 13·2—Victor Meyer's Apparatus.

Calculations. The volume of air measured above is reduced to *N.T.P.* Let *w* gm. of the substance liberate *V* ml. of air at *N.T.P.* Weight of the substance that will liberate 22·4 litres of air at *N.T.P.* is calculated. This gives the mol. wt. of the volatile substance. Thus

$$\text{Mol. wt.} = \frac{w \times 22,400}{V}$$

In case vapour density is to be calculated it is half of the mol. wt. calculated above. It may, however, be directly calculated as shown on the next page.

Example 2. *The speeds of diffusion of carbon dioxide and of ozone were found to be 0·58 : 0·542 ; find the molecluar weight of ozone if that of carbon dioxide is known.*

r_1 for carbon dioxide	=0·58
r_2 ,, ozone	=0·542
M_1 ,, carbon dioxide (CO_2)	=12+32=44
M_2 ,, ozone	=?

Applying Graham's law :

$$\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}$$

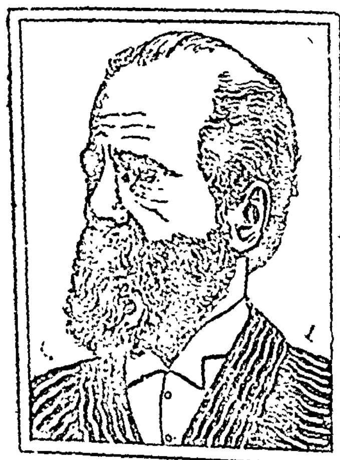
we have

$$\frac{0·58}{0·542}=\sqrt{\frac{M_2}{44}}$$

or

$$\left(\frac{0·58}{0·542}\right)^2=\frac{M_2}{44}$$

whence $M_2=\frac{0·58\times0·58\times44}{0·542\times0·542}=50·39.$



Victor Meyer
(1865—97)
German chemist known for the method known after his name for the determination of molecular weights of volatile substances.

4. **Molecular Weights of Volatile Substances.**—Molecular weights of volatile liquids and solids can be easily determined by coverting a known weight (say, *w* gm.) of the substance into vapour. The volume of vapour obtained is measured under atmospheric conditions and then reduced to *N.T.P.* (say=*v* ml.). Therefore, the weight of 22,400 ml. of the vapour is calculated. This gives the molecular weight. Different methods employed are :

(a) Victor Meyer's Method.

Apparatus Used. Victor Meyer's apparatus used for determining the molecular weight of a volatile substance is shown in Fig. 13·2. It consists of an inner Victor Meyer' tube, *A*, provided with funnel, *F*, at the top, a bulb at the bottom and side tube, S, near the upper end. The top is fitted with a rubber stopper while the lower end is surrounded by a jacket, *J*, containing a liquid of b. p. about 20°C higher than the volatilization temperature of the volatile substance. The bottom of the bulb inside is covered with glass wool or asbestos fibre. The side tube is dipping under water in a trough.

Procedure. The experiment is carried out as follows :

(i) Boil the liquid in the outer jacket when the side tube is [illegible] more air bubbles are evolved. This [illegible] the tube is uniform.

(*ii*) Invert a graduated tube, *G*, filled with water over bee-hive shelf.

(*iii*) Weigh out accurately some volatile substance in a Hofmann's bottle, *H*, with a tiny stopper.

(*iv*) Remove the stopper from *F* for a second, slip in the tiny bottle and replace the stopper immediately. As soon as it reaches the bottom, the volatile substance vaporizes and blows off the tiny stopper. The shape of the tube is such that the vapour pushes an equal volume of air into the graduated tube.

(*v*) After careful levelling, note down the volume, temperature and pressure of the air collected. For levelling, the graduated tube, partly filled with the air collected, is lowered *into* a tall jar containing water till the inside level is the same as the outside level (Fig. 13·3). The volume thus noted is the volume of air at atmospheric pressure.

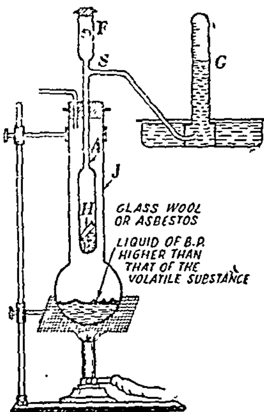


Fig. 13·2—Victor Meyer's Apparatus.

Calculations. The volume of air measured above is reduced to *N.T.P.* Let w gm. of the substance liberate V ml. of air at *N.T.P.* Weight of the substance that will liberate 22·4 litres of air at *N.T.P.* is calculated. This gives the mol. wt. of the volatile substance. Thus

$$\text{Mol. wt.} = \frac{w \times 22{,}400}{V}$$

In case vapour density is to be calculated *it is half* of the mol. wt. calculated above. It may, however, be directly calculated as shown on the next page.

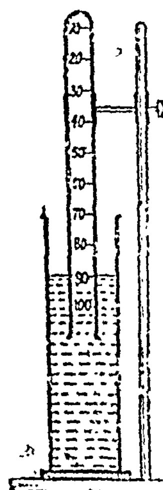


Fig. 13·3—Measuring the volume after careful levelling.

$$V.D.=\frac{\text{Wt. of } V \text{ ml. of vapour at } N.T.P.}{\text{Wt. of } V \text{ ml. of hydrogen at } N.T.P.}$$

$$=\frac{w}{V\times \cdot 00009} \text{ approximately.}$$

or $$V.D.=\frac{w}{V\times 2/22{,}400}=\frac{w\times 22{,}400}{V\times 2} \text{ accurately.}$$

Example 3. *0·22 gm. of a substance when vaporised, displaced 45·0 c.c. of air measured over water at 20°C and 755 mm. pressure. Calculate the molecular weight of the substance. [Aq. tension at 20°C=17·4 mm.]*

(a) Reducing the volume of air collected, at N.T.P.

V_1=45 c.c. V_2=?

P_1=755−17·4=737·6 mm. P_2=760 mm.

T_1=273+20 =293° Abs. T_2=273° Abs.

$$V_2=\frac{P_1V_1}{T_1}\times\frac{T_2}{P_2}=\frac{737\cdot6\times45\times273}{293\times760}=40\cdot7 \text{ c.c.}$$

(b) Calculation of Mol. wt.

Wt. of substance taken=0·22 gm.

Wt. of substance that will liberate 22·4 litres of air at *N.T.P.*

or gm. mol. wt.$=\frac{0\cdot22\times22{,}400}{40\cdot7}$=121·1 gm.

∴ Mol. wt. of substance=121·1.

Example 4. *0·1 gm. of a volatile substance on vaporization in Victor Meyer's apparatus displaced 27 c.c. of moist air measured at 15°C and 740 mm. pressure. Calculate the molecular weight of the substance. [Aqueous tension at 15°C=12·7 mm.]*

(a) Reducing the volume of air collected to N.T.P.

V_1=27 c.c. V_2=?

P_2=740−12·7=727·3 mm. P_2=760 mm.

T_1=15+273 =288° Abs. T_2=273° Abs.

$$V_2=\frac{P_1V_1T_2}{T_1P_2}=\frac{727\cdot3\times27\times273}{788\times760}=24\cdot50 \text{ c.c.}$$

(b) Calculation of Mol. wt.

Wt. of 24·5 c.c. of the vapour at *N.T.P.*=0·1 gm.

,, 22·4 litres ,, ,, (*i.e.*, 1 gm. mol. wt.)

$$=\frac{0\cdot1}{24\cdot5}\times22{,}400=91\cdot43 \text{ gm.}$$

∴ Mol. wt. of the substance=91·43.

(*b*) **Duma's Method.** Duma's bulb employed in this method is a glass bulb of about 200 ml. capacity. It is provided with a long drawn out neck (Fig. 13'4). The bulb is dried and weighed when full of air. Let the weight be w_1 gm. A small quantity of the volatile liquid is introduced into the bulb by alternate heating and cooling. The bulb is now clamped in a suitable bath maintained at a temperature about 20° higher than the b.p. of the liquid. The liquid vaporizes and drives out the air completely. The bulb is sealed off when no more of vapour comes out. The temperature of the bath is noted and the bulb is weighed full of vapour. Let the weight be w_2 gm.

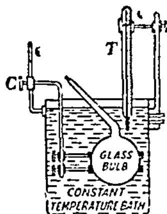


Fig. 13'4—Duma's method.

To find the capacity of the bulb, its neck is broken and it is filled with pure distilled water. The bulb is then weighed full of water. The weight of water contained in grams gives the capacity of the bulb in ml.

Calculations. Knowing the capacity of the bulb we can calculate the volume of air contained in it during first weighing and volume of vapour during second weighing and can reduce them to *N.T.P.* Let it be V_1 and V_2 ml. respectively at *N.T.P.*

Wt. of empty globe $= W_1 -$ Wt. of air $= W_3$ (say)

Wt. of vapour $= W_2 - W_3 = W_4$ (say)

Now $$\text{V.D.} = \frac{\text{Wt. of } V_2 \text{ ml. of vapour at } N.T.P.}{\text{Wt. of } V_2 \text{ ml. of hydrogen at } N.T.P.}$$

$$= \frac{W_4}{V_2 \times \cdot 00009}$$

5. **Molecular Weights of Non-Volatile substance.**— Every liquid freezes and boils at fixed temperatures and the effect of addition of a solute to it is such as to take the two fixed points farther from each other, *i.e.*, the freezing point is lowered while the boiling point is raised. The depression of freezing point or elevation of boiling point is, however, found to be proportional to the amount of the solute added to a known weight of the solvent. This is used in the determination of molecular weights of non-volatile substances. The two methods employed are .

(*a*) **Depression of Freezing-point Method.** *Depression in freezing point of a solvent produced by dissolving 1 gm. mol. wt. of any solute in 100 gm. of the solvent is called its* **Molecular Depression Constant (K).** For example, molecular depression constant for water $= 18 \cdot 6$, *i.e.*, dissolution of 1 gm. mol. wt. of any

solute in 100 gm. of water produces a depression of 18·6°C in its freezing point.

The depression in freezing point ($=\Delta T$) noted experimentally by dissolving w gm. of solute (mol. wt.$=M$) in W gm. of the solvent, is related to its molecular depression constant, K as given below :

$$m=\frac{100\,Kw}{\Delta TW}.$$

The molecular depression constants for some common solvents are given below :

Water	=18·6	Benzene	=51·2
Acetic acid	=39	Phenol	=53

Example 5. *1·5 gm. of a substance when dissolved in 60 gm. of water lowered the freezing point by 0·136°C. The depression constant of water is 18·6. Calculate the molecular weight of the substance.*

Putting down the data :

Wt. of the substance	$(w)=1{\cdot}5$ gm.
,, ,, ,, solvent	$(W)=60$ gm.
Depression of F. pt.	$(\Delta T)=0{\cdot}136°C$
Mol. depression constant	$(K)=18{\cdot}6$
Mol. wt. of the solute	$(m)=?$

Substituting these values in the relation :

$$m=\frac{100\,Kw}{\Delta TW},$$

we have

$$m=\frac{100\times 18{\cdot}6\times 1{\cdot}5}{0{\cdot}136\times 60}=341{\cdot}9$$

∴ **Mol. Wt. of the substance** $=341{\cdot}9$.

(b) Elevation of Boiling-point Method. *Elevation in boiling point of a solvent produced by dissolving 1 gm. mol. wt. of any solute in 100 gm. of the solvent is called its* **Molecular Elevation Constant** *(K).* For example, molecular elevation constant of water is 5·2, *i.e.*, dissolution of 1 gm.-mol. wt. of any solute in 100 gm. of water produces an elevation of 5·2°C in its boiling point.

The elevation in boiling point ($=\Delta T$) noted experimentally, by dissolving w gm. of the solute (mol. wt.$=m$) in W gm. of the solvent, is related to its molecular elevation constant K as given below :

$$m=\frac{100\,Kw}{\Delta TW}.$$

The molecular elevation constants for some common solvents are given below :

Water	= 5·2	Acetone	=17·2
Benezene	=25·7	Chloroform	=38·8
Ether	=21·1	Ethyl alcohol	=11·5

Example 6. *The boiling point of pure acetone is 56·38° at normal pressure. A solution of 0·707 gm. of a compound in 10 gm. of acetone boils at 56·88°. What is the molecular weight of the compound? [K for acetone=16·7.]*

Weight of the solute $(w)=0·707$ gm.

,, ,, solvent, acetone $(W)=10·0$ gm.

Elevation of Boiling Point $(\Delta T)=(56·88-56·38)=0·5$°C

Molecular elevation constant $(K)=16·7$

Mol. wt. of the compound $(m)=?$

Substituting these values in the relation,

$$m=\frac{100\,Kw}{\Delta T W},$$

we get
$$m=\frac{100\times 16·7\times 0·707}{0·5\times 10}=236·1.$$

Mol. wt. of the compound $=236·1$.

QUESTIONS AND PROBLEMS

Essay type Questions

1. (a) Explain the meaning of :
   (i) Molecular weight of substance
   (ii) Gram molecular weight.
   (iii) 'Gram-molecular volume'.
   (Delhi H.S 1968 ; Punjab H S. 1964 ; Pre-Univ. 1964)

   (b) How is molecular weight related to vapour density ?
   (Punjab Inter. 1960)

2. Describe Victor Meyer's method of determining the molecular weight of a volatile liquid. *(Punjab Pre-Univ. & H S 1964 ; Delhi H S 1965, 62 ; Nagpur Pre-University 1971, 70)*

3. In the Victor Meyer's method for the determination of molecular weights, account for the following :
   (i) For what type of substance is the method applicable ?
   (ii) What type of compound should be selected for the vapour bath (the outer metallic jacket) and why ?
   (iii) Why is a layer of sand or asbestos placed at the bottom of the bulb in the Victor Meyer's tube ?
   (iv) *What is collected in the graduated tube after the substance has volatilized ?*
   (v) Why is levelling of water in the graduated tube necessary before the volume is finally read ? *(Punjab Pre-University 1971)*

4. What is meant by the term "Vapour Density" ? Describe methods for finding the molecular weight of a gas such as nitrogen.

5. What are the important methods for the determination of molecular weights ? Give experimental details for one of the methods.

Molecular Weight of Gases

6. The weight of 5600 c.c. of a gas at N.T.P. is 12 gm. What is the molecular weight of the gas ? *(Bombay Inter. 1963 Supp.)*

7. 4·86 litres of carbon dioxide at 12°C and 770 mm. pressure weighs 9·27 gm. Calculate the molecular weight of the gas ? (*Senior Cambridge 1965*)

8. One litre of a gas at N.T.P. weighs 1·52 gm. What is its molecular weight ? (*Senior Cambridge 1964 Dec.*)

9. Volume of 1·7 gm. of a gas at 0°C and 760 mm. pressure is 2·24 litres. Calculate its molecular weight and vapour density. (*Senior Cambridge 1964 July*)

10. 0·656 gm. potassium chlorate on heating gave 0·286 gm. potassium chloride and liberated 278 c.c. oxygen at 20°C and 760 mm. pressure. Calculate the molecular weight of oxygen. (*Senior Cambridge 1962 Nov.*)

11. 24·16 c.c. of a gas at 25°C and 740·3 mm. pressure weigh 0·11 gm. Calculate the molecular weight of the gas. (*All India H.S. 1967*)

12. Determine the molecular weight of a gaseous compound, 1·00 gm. of which occupy 800 c.c. at N.T.P. (*Nagpur Pre-University 1970*)

Molecular Weight of Volatile Compounds

13. In a Victor Meyer's determination 0·0926 gm. of a liquid gave 28·9 c.c. of a gas collected over water at 16°C and 753·5 mm. pressure. Find the vapour density and molecular weight of the substance. [*Aq. tension at 16°C is 13·5 mm.*] (*Delhi H.S. 1962*)

14. 0·2335 gm. of a liquid when vaporised completely, displaced 37·10 c.c. of air measured at 29°C and 743 mm. pressure. Calculate the mol. wt. of the liquid. [*Aq. tension at 29°C is 29·7 mm. of Hg.*] (*Nagpur Pre-University 1970*)

15. 0·1008 gm. of chloroform expelled 20·0 c.c. of air at 15°C and 757 mm. pressure. Calculate its molecular weight. (*Bombay Inter. 1963*)

16. In a determination of vapour density by Victor Meyer's method 0·406 gm. of a substance expelled 170 c.c. of air, measured over water at 15·1°C and 763 mm. pressure. Find the molecular weight of the substance. [*Aqueous tension at 15·1°C is 13 mm.*]

17. In Victor Meyer's method 0·309 gm. of the vapour of a volatile liquid displaced 488 ml. of dry air at 23°C and 737 mm. pressure. Calculate the molecular weight. The compound contains only carbon and hydrogen. Suggest the probable molecular formula of the compound. (*Punjab Pre-University 1971*)

18. 0·1 gm. of a volatile substance on vaporisation displaced 27 c.c. of air measured over water at 15°C and 740 mm. pressure. Calculate the molecular weight of the substance. [*Aqueous tension at 15°C is 13 mm.*] (*Nagpur Pre-University 1971*)

19. 0·02 gm. of ether when heated in a Victor Meyer's apparatus expelled 8·0 c.c. air measured at 30°C and 742 mm. pressure over water. Find the mol. wt. of ether. [*Aqueous tension at 30°C is 32 mm.*]

20. In Victor Meyer's determination 0·23 gm. of a substance displaced air which measured 112 c.c. at N.T.P. Calculate the vapour density and molecular weight of the substance. [*1 litre of H_2 at N.T.P. weighs 0·09 gm.*]

Molecular Weights of Non-volatile Compounds

21. The freezing point of water was lowered by 0·19°C by dissolving 0·152 gram of the substance in 25 grams of water. Calculate the molecular weight of the substance.

[*Molecular depression constant of water for 100 grams=18·5*].

22. 1·5 gm. of a substance when dissolved in 60 gm. of water lowered the freezing point by 0·136°C. The depression constant for water is 18·6. Calculate the molecular weight of the substance.

23. 13·6 gm. of a substance when dissolved in 20 gm. of water causes a depression in F. pt. of 3·7°C. Calculate the molecular weight. [*K for water* =*18·5°C.*] (*Rajasthan Inter. 1965*)

Miscellaneous

24. Calculate the volume of 0·22 gm. of CO_2 at 570 mm. and 0°C. (*Madhya Pradesh Inter. 1964*)

25. 5·40 gm. of glucose ($C_6H_{12}O_6$) dissolved in 120 gm. water raised the boiling point by 0·13°C. Calculate the molecular elevation constant for water. (*Bombay Inter. 1961*)

Test Your Understanding

26. (*a*) What is the actual weight of a molecule of sulphur dioxide and its molecular weight ? (*Guru Nanak Pre-Univ. 1971*)

(*b*) 112 ml. of a gas at N.T.P. weighs 0·15 gm. What is its mol. wt. ?

(*c*) A gas diffuses twice more rapidly than methane (CH_4) Calculate its mol. wt.

(*d*) Fill in the blanks :

(i) Molecular weight of a substance is the .....weight of its molecule as compared with the weight of an atom of . . (..isotope) taken as .....

(ii) Weight of a substance in grams numerically equal to its molecular weight is termed its .....

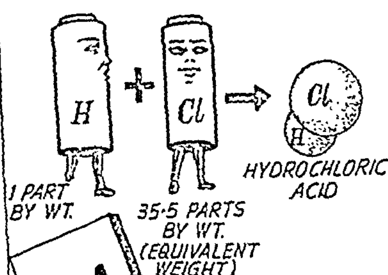
(iii) The weight of a volume of gas divided by the weight of an equal volume of hydrogen (at the same temperature and pressure) is equal to the .....

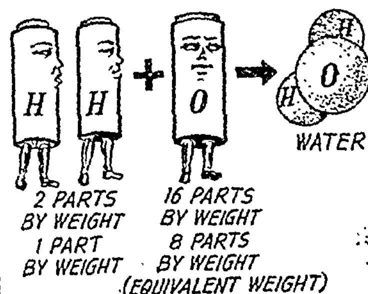
KEY

(*a*) ($64/6·02\times10^{23}$) gm. ; 64 (*b*) 30 (*c*) 4 (*d*) (i) relative, carbon, C^{12}, 12 amu. (ii) gram-molecular weight. (iii) vapour density.

ANSWERS

6. 48.	7. 44·01.	8. 34·04.	9. 17, 8·5.
10. 32.	11. 114.	12. 28	13. 39 ; 78.
14. 166·2.	15. 119·5.	16. 57·2.	17. 16·07 ; CH_4.
18. 91·45.	19. 66·49.	20. 22·82 ; 45·64.	21. 59·2.
22. 341·9.	23. 340·0.	24. 149·3 c.c.	25. 5·2.





Equivalent Weights

1. **What is Equivalent Weight ?**—In our daily life we a used to the idea of exchange value. Thus for one rupee we c exchange 4 lead pencils or 12 oz. sweets or 6 ices. Since these articl are all related (in value) to one r pee, they are related to one anoth Thus we can exchange 4 lead penc for 6 ices or for 12 oz. of sweets. other words, they are exactly eq valent to each other.

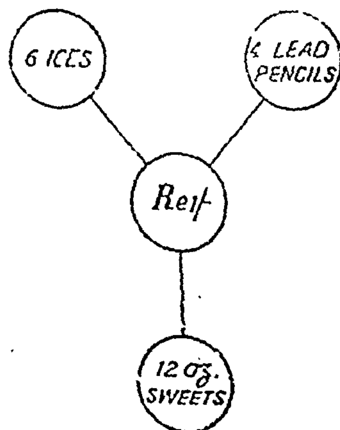


Fig. 14·1.

The whole idea of equival weights in chemistry is very simi in conception. It is a chemical r of exchange and the chemical ruj or *reference unit is unit weight hydrogen.*

Hydrogen is liberated by action of metals like zinc, mag sium or iron on dilute sulphu acid. To liberate one gram of hyd gen we require 12 gm. of magnesium or 33 gm. of zinc or 28 g of iron.

In other words, 1 gm. of hydrogen is equivalent to 12 gm. magnesium or 33 gm. of zinc or 28 gm. of iron. 12, 33 and 28 termed equivalent weights of magnesium, zinc and iron respectiv

One gram of hydrogen combines with 8 gm. of oxygen to give water and 35·5 gm. of chlorine to produce hydrochloric acid. From this, equivalent weights of oxygen and chlorine are 8 and 35·5 respectively.

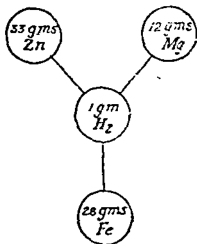


Fig. 14·2.

In addition to unit weight of hydrogen, 8 parts by weight of oxygen and 35·5 parts by weight of chlorine have also been used as reference units in this chemical rate of exchange.

2. Equivalent Weight is a Number.—*Equivalent weight of a* [illegible] *1·008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine. It is only a number.*

For example, (i) 16 parts by weight of sulphur combine with *1·008 parts by weight of hydrogen in* H_2S ; the equivalent weight of sulphur is, therefore, 16.

(ii) 12 parts by the weight of magnesium combine with 8 parts by weight of oxygen in MgO ; this gives the equivalent weight magnesium as 12.

(iii) 108 parts by weight of silver combine with 35·5 parts by weight of chlorine to show that equivalent weight of silver is 108.

(*iv*) 49 parts by weight of sulphuric acid liberate 1·008 parts by weight of hydrogen when treated with a metal ; therefore, the equivalent weight of sulphuric acid is 49.

3. Gram-Equivalent Weight.—Weight of a substance in grams numerically equal to the equivalent weight, is called *gram-equivalent weight or gram equivalent* of the substance. The following examples will illustrate the point :

(i) Equivalent weight of sulphuric acid is 49 ; therefore 49 gm. by weight of sulphuric acid is its gram-equivalent weight.

(ii) Equivalent weight of caustic soda (NaOH) is 40 while its gram-equivalent weight is 40 gm.

4. Equivalent Weight may vary.—As given above, equivalent weight of any element is determined by analysis of its compounds with hydrogen, oxygen or chlorine. In case an element forms more than one oxide or chloride, its equivalent weight naturally varies. For example, copper gives two oxides, *viz.*, cuprous oxide, Cu_2O and cupric oxide, CuO.

Here 8 parts by weight of oxygen combine with 63·6 parts by weight of copper in cuprous oxide and 31·8 parts by weight of

copper in cupric oxide. Consequently the equivalent weight of copper in cuprous oxide and cupric oxide are 63·6 and 31·8 respectively.

Similarly, equivalent weight of iron in ferrous oxide and ferric oxide are 27·9 and 18·6 respectively. Thus equivalent weight of an element varies with valency according to the relation:

$$\text{Equivalent weight} = \frac{\text{Atomic weight}}{\text{Valency}}.$$

Now atomic weight is constant but valency is variable; equivalent weight is, therefore, variable.

5. **Determination of Equivalent Weight of Metals.**— Different methods employed for the determination of equivalen weight of metals are :

(1) **Hydrogen Displacement Method.** A known weight o a metal (say, w gm.) is treated with an excess of diluted acid and the volume of hydrogen evolved is measured after careful levelling. The volume of hydrogen is reduced to N.T.P. (say, it is v ml.) *Equivalent weight of metal is the weight of the metal that wil liberate 11·2 litres of hydrogen at N.T.P.*, this being the volume occupied by 1·008 gm. (1 gm. eq. wt.) of hydrogen.

$$\text{Eq. wt. of the metal} = \frac{w}{v} \times 11{,}200.$$

In cases where wt. of 1 ml. of hydrogen is given the weight of v ml. of H_2 at N.T.P. is calculated (say, it is z gm.). This is the weight of hydrogen displaced by w gm. of the metal. From here Eq. wt. of the metal

$$= \frac{w}{z} \times 1{\cdot}008.$$

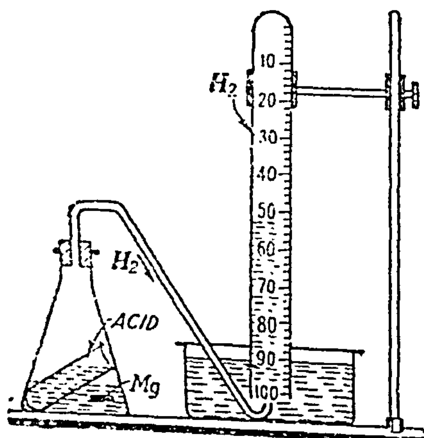


Fig. 14·3—Equivalent weights of metals by hydrogen displacement method.

The apparatus used is shown in the diagram (Fig. 14·3). A known weight of the metal is placed in a conical flask fitted with a cork and delivery tube. The metal is covered with a layer of water and a test tube containing sulphuric or hydrochloric acid is lowered. The flask is corked and a graduated tube full of water is placed in position on the bee-hive shelf.

The test tube containing the acid is now tilted when the acid mixes with water and reacts with the metal. Hydrogen gas is liberated and collects in the graduated tube. When the reaction is over and no more hydrogen collects in the graduated tube, it is removed and volume of hydrogen collected is noted after careful levelling.

Example 1. *0·218 gm. of magnesium displaced 218·2 c.c. of hydrogen measured at 754·5 mm. pressure and 17°C from a dilute hydrochloric acid solution. Calculate the equivalent weight of the metal. (Aqueous tension at 17°C=14·4 mm.)*

(*Nagpur Pre-University 1971*)

(*a*) *Reducing the volume of hydrogen evolved to N.T.P.*

V_1=218·2 c.c.	V_2=?
P_1=754·5−14·4=740·1 mm.	P_2=760 mm.
T_1=17+273=290° Abs.	T_2=273° Abs.

$$V_2=\frac{P_1V_1T_2}{T_1P_2}=\frac{740{\cdot}1\times218{\cdot}2\times273}{290\times760}=200{\cdot}1 \text{ c.c.}$$

(*b*) *Calculation of Equivalent weight :*

Wt. of the metal which displaces 200·1 c.c. of hydrogen at N.T.P.=0·218 gm.

Wt. of the metal which displaces 11·2 litres of hydrogen at

$$\text{N.T.P.}=\frac{0{\cdot}218}{200{\cdot}1}\times11{,}200=12{\cdot}20 \text{ gm.}$$

∴ Equivalent weight of the metal=12·20.

...al (=w_1, ... case of ... f copper ... obtained ... stopped when the weight of oxide (=w_2, say) is constant.

From this data, the equivalent weight which is the weight of the metal that combines with 8 parts by weight of oxygen is calculated.

Calculations. Wt. of metal taken=w_1 gm.

Wt. of metal oxide obtained=w_2 gm.

„ „ oxygen combined =w_2-w_1 gm.

Now (w_2-w_1) gm. of oxygen combines with w_1 gm. of the metal.

$$\therefore \quad \text{Eq. wt. of the metal}=\frac{w_1}{w_2-w_1}\times8.$$

Example 2. *3·5 gm. of copper were dissolved in excess of concentrated nitric acid, and the nitrate thus formed was ignited to form the oxide. The weight of the oxide obtained was 4·5 gm. Find the equivalent weight of copper.*

Weight of copper taken	=3·5 gm.
„ „ oxide obtained	=4·5 gm.
„ „ oxygen combined	=4·5−3·5=1 gm.

1 gm. of oxygen combines with 3·5 gm of copper.

8 gm. of oxygen combines with 3·5×8=28 gm. of copper.

∴ Equivalent wt. of copper=28.

(3) **Reduction of Oxide Method.** In certain cases the metal oxide can be easily reduced to the metallic state by heating in a current of hydrogen or coal gas, *e.g.*, copper oxide. In such cases a known weight of the oxide is reduced to the metallic state by heating in a current of hydrogen, etc., and the metal obtained is weighed. From the weight of the metal obtained and the oxide taken equivalent weight of the metal is calculated as in *Example 2.*

Example 3. *A current of dry hydrogen was passed over 2·37 gm. of heated black oxide of copper when 1·89 gm. of copper were obtained. Find the equivalent weight of copper.*

Weight of copper oxide taken =2·37 gm.
" " metallic copper obtained =1·89 gm.
" " oxygen removed =2·37−1·89=0·48 gm.

Now 0·48 gm. of oxygen combines with 1·89 gm. of copper.

or 8 gm. of oxygen combines with $\frac{1 \cdot 89}{0 \cdot 48} \times 8 = 31 \cdot 5$ " " "

∴ **Equivalent weight of copper=31·5.**

(4) **By Combination with Chlorine.** Metals like gold and silver do not liberate any hydrogen from acids, nor do they form any oxide. These can, however, be easily converted into their chlorides. Their equivalent weights are determined by combination with chlorine method. A known weight of the metal is converted into its chloride by direct treatment with chlorine or an indirect method (*e.g.*, in case of silver, it is first dissolved in nitric acid and then precipitated with dilute hydrochloric acid). From the weight of metal taken and chloride obtained, the weight of the metal which combines with 35·5 parts by weight of chlorine is calculated.

Example 4. 0·54 *gm. of silver, dissolved in nitric acid, gave on addition of a solution of common salt* 0·7175 *gm. of silver chloride. Determine the equivalent weight of silver.*

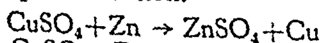
Weight of silver taken =0·54 gm.
" " " chloride obtained =0·7175 gm.
" " " chlorine combined =0·7175−0·54
=0·1775 gm.

Now 0·1775 gm. of chlorine combines with 0·54 gm. of silver
35·5 gm. chlorine will combine with

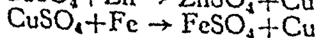
$$\frac{0 \cdot 54}{0 \cdot 1775} \times 35 \cdot 5 = 108 \text{ gm. of silver.}$$

∴ **Equivalent weight of silver=108.**

(5) **Metal Displacement Method.** A more electropositiv[e] metal displaces another less electropositive metal from its sal[t] solution, *e.g.*, zinc, magnesium or iron displaces copper whe[n] placed in copper sulphate solution.



$$CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$$



$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

The displacement takes place in equivalent amounts and i[s] used for the determination of equivalent weights of metals lik[e]

magnesium, zinc, copper, silver and iron. A known weight of the metal, say magnesium, is placed in a solution of another salt like copper sulphate and the metal displaced is washed, dried and weighed.

Knowing the equivalent weight of one of the two metals, that of the other is calculated.

$$\frac{\text{Eq. wt. of magnesium}}{\text{Eq. wt. of copper}}=\frac{\text{Wt. of magnesium taken}}{\text{Wt. of copper precipitated}}$$

Example 5. *1·081 gm. of copper displaced 3·670 gm. of silver from a solution of silver nitrate. Find the equivalent weight of copper.* [*Ag*=*107·88.*]

Here : Wt. of copper added =1·081 gm.
Wt. of silver precipitated =3·670 gm.
Eq. wt. of silver =107·88.

Substituting these values in the equation :

$$\frac{\text{Wt. of copper added}}{\text{Wt. of silver precipitated}}=\frac{\text{Eq. wt. of copper}}{\text{Eq. wt. of silver}}$$

we have $$\frac{1·081}{3·670}=\frac{\text{Eq. wt. of copper}}{107·88}$$

whence $$\text{Eq. wt. of copper}=\frac{1·081}{3·670}\times 107·88=31·77.$$

(6) **Double Decomposition Method.** In this method a known weight of salt *AB* (say, w_1 gm.) is dissolved in water and treated with excess of another salt, *CD*, when a third salt, *BC*, is precipitated. This is filtered, washed, dried and weighed (say, its weight is w_2 gm.). Weights of *AB* and *BC* are in the ratio of their equivalent weights. Further, the equivalent weight of a salt is the sum of the equivalent weights of its two radicals, *e.g.*,

Eq. wt. of *AB*, E_{AB}=Eq. wt. of *A*, E_A+Eq. wt. of *B*, E_B.

Applying the relationship between weights and equivalent weights of *AB* and *BC*, we have

$$\frac{\text{Wt. of } AB}{\text{Wt. of } BC}=\frac{\text{Eq. wt. of } AB}{\text{Eq. wt. of } BC}=\frac{\text{Eq. wt. of } A+\text{Eq. wt. of } B}{\text{Eq. wt. of } B+\text{Eq. wt. of } C}\cdot$$

or $$\frac{w_1}{w_2}=\frac{E_{AB}}{E_{BC}}=\frac{E_A+E_B}{E_B+E_C}\cdot$$

Knowing the equivalent weights of any two radicals from *A*, *B*, *C*, that of the third can be calculated.

Ex. [illegible] *metal dissolved in water* [illegible] *solution. The weight of* [illegible] *hing and drying was found to be 2·87 grams. Calculate the equivalent weight of the metal.*

Here : Wt. of metal chloride=1·11 gm.
,, silver chloride=2·87 gm.
Eq. wt. of silver =108
Eq. wt. of chloride radical =35·5
Let the Eq. wt. of metal be $=x$

Substituting these values in the following equation :

$$\frac{\text{Wt. of metal chloride}}{\text{Wt. of silver chloride}}=\frac{\text{Eq. wt. of metal chloride}}{\text{Eq. wt. of silver chloride}}$$

we have, $$\frac{1·11}{2·87}=\frac{x+35·5}{108+35·5}=\frac{x+35·5}{143·5}$$

or $$x+35·5=\frac{1·11}{2·87}\times 143·5=55·5$$

whence $$x=55·5-35·5=20·0$$

∴ Eq. wt. of the metal=20·0.

(7) **By Electrolysis.** The method is based on Faraday's **Second Law of Electrolysis** which states : *When the same current passes through different electrolytes, the weights of different ions liberated are in the ratio of their equivalent weights.*

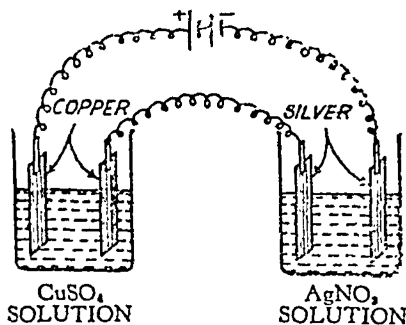


Fig. 14·4—Equivalent weight of a metal by electrolysis.

An electric current is passed through different voltmeters (say, containing copper sulphate and silver nitrate solutions) and the weights of ions deposited (copper and silver in this case) are determined. Then

$$\frac{\text{Wt. of copper deposited}}{\text{Wt. of silver deposited}}=\frac{\text{Eq. wt. of copper}}{\text{Eq. wt. of silver}}$$

Knowing the Eq. wt. of one, that of the other can be calculated.

Example 7. *The passage of a current of electricity through acidulated water and solution of copper sulphate liberated 203 c.c. of hydrogen at N.T.P. and deposited 0·571 gram of copper. Calculate the equivalent weight of copper.*

Volume of hydrogen liberated=203 c.c. at N.T.P.
Weight of ,, ,, ,, =203×·00009 =0·1827 gm.
Wt. of copper deposited =0·571 gm.

Substituting these values in the relation

$$\frac{\text{Wt. of copper}}{\text{Wt. of hydrogen}}=\frac{\text{Eq. wt. of copper}}{\text{Eq. wt. of hydrogen}}$$

we get $$\frac{0·571}{0·01827}=\frac{x}{1·008}$$

whence $$x=\frac{0·571}{0·01827}\times 1·008=31·5$$

∴ Eq. wt. of copper=31·5.

6. **Determination of Equivalent weights of Non-metals.**— Chief methods employed for the determination of equivalent weights of non-metals are :

(1) **Combination with Hydrogen.** Weighed quantity of hydrogen is burnt in chlorine to give hydrochloric acid which can

be weighed. From these the weight of chlorine combining with 1·008 parts by weight of hydrogen is its equivalent weight.

[illegible] over weighed quantity [illegible] can be absorbed in a [illegible] of cupric oxide is the weight of oxygen (= w_1, say) combined with hydrogen. Increase in weight of $CaCl_2$ tube gives the weight of water produced (= w_2, say). Weight of hydrogen combined is, therefore, $w_2 - w_1$. From this the weight of oxygen that combines with 1·008 parts by weight of hydrogen, is the equivalent weight of oxygen.

(2) **Combination with Oxygen.** For example, to determine equivalent weight of sulphur, a weighed quantity of it (say, w_1 gm.) is burnt in a current of oxygen and sulphur dioxide produced is absorbed in weighed potash bulbs. Increase in weight of potash bulbs gives the weight of sulphur dioxide (say, w_2 gm.). Weight of oxygen that combines with w_1 gm. of sulphur is $(w_2 - w_1)$ gm.

From here Eq. wt. of sulphur $= \frac{w_1}{w_2 - w_1} \times 8$

(3) **Combination with Chlorine.** Equivalent weights of phosphorus, arsenic, etc., are determined by this method. Calculations are just as given for metals.

(4) **Double Decomposition Method** The equivalent weight of a non-metallic radical is determined in the same way as that of a metallic radical.

[illegible] ights of [illegible] dis- cus[illegible]

Equivalent weights of substances are also calculated with the help of the **Law of Equivalent Proportions** according to which *substances react in the ratio of their equivalent weights.* For example, equivalent weights of NaOH, H_2SO_4 are 40 and 49 respectively. 40 grams of NaOH neutralize exactly 49 grams of H_2SO_4 and 80 grams of NaOH will neutralize 98 grams of H_2SO_4.

Example 8. *A 5 gm. sample of an acid was dissolved in water and an excess of zinc was added. The weight of the evolved hydrogen was 0·0667 gm. Calculate the equivalent weight of the acid. What is the weight of sodium hydroxide that would neutralize 9·00 gm. of this acid?* [H=1·00; Na=23; O=16] (Delhi H S. 1966)

0·0667 gm. of hydrogen are liberated from 5 gm. of the acid.

Weight of the acid that will liberate 1 gm. (1 gm. eq wt.) of hydrogen $= \frac{5}{0·0667} = 74·96$ gm.

∴ Eq. wt. of the acid = 74·96.

40 gm. (1 gm. eq. wt.) of sodium hydroxide will neutralize 74·96 gm. (1 gm. eq. wt.) of this acid.

∴ Wt. of NaOH which will neutralize 9 gm. of this acid

$$= \frac{40}{74·96} \times 9 = 4·802 \text{ gm.}$$

QUESTIONS AND PROBLEMS

Essay-type Questions

1. Define and *illustrate the equivalent* weight of an element. Name four simple methods for the determination of equivalent weights of metals. Describe a method for determining the equivalent weight of the metal. *(Delhi H.S. 1965 ; Bihar 1965 Supp.)*

2. (*a*) What *do you understand by the term* equivalent weight ? Discuss the method of determining the equivalent weight of zinc, magnesium or copper. *(Nagpur Pre-Univ. 1971 ; Punjab H.S. 1968 ; Bihar 1964 Supp.)*

(*b*) Define equivalent weight of an element. Distinguish between equivalent weight of *hydrogen and gram equivalent* weight of hydrogen. Give briefly the method of procedure and method of calculation for determining the equivalent weight of a metal by the hydrogen displacement method. *(Punjab Pre-Univ. 1962)*

(*c*) Write a *short note on the application of the phenomenon* of electrolysis for determining the equivalent weights of metals. *(Punjab Pre-Univ. 1963)*

(*d*) Define Eq. wt. of a base. *(Delhi H.S. 1968)*

(*e*) How would you proceed to determine the equivalent weight of an acid ? *(Delhi H.S. 1964)*

[Hint. Treat a known weight of the acid with excess of zinc as in Hydrogen Displacement Method, *page* 1·131, and measure the volume of hydrogen evolved. One gram equivalent of the acid will liberate one gram equivalent of hydrogen (=1·008 gram). Suppose *W* gram of the acid on treatment with excess of zinc liberates *w* gram of hydrogen. Calculate the weight of acid which will liberate 1·008 gm. of hydrogen. This will give 1 gm. eq. wt. of the acid.

$$\text{Gm. eq. wt. of the acid} = \frac{W}{w} \times 1{\cdot}008 \text{ gm.}$$

$$= E \text{ gm. (say)}$$

$$\therefore \text{ Eq. wt. of the acid} = E.]$$

Hydrogen Displacement Method

3. 0·33 gm. of a metal gave on treatment with a dilute mineral acid 113 c.c. of hydrogen measured at N.T.P. Calculate the equivalent weight of the metal. *(Delhi H.S. 1965)*

4. 0·45 gm. of a metal gave 176·6 c.c. of hydrogen at 23°C and 743 mm pressure when treated with dilute sulphuric acid. Calculate the equivalent weight of the metal. *[Aqueous tension at 23 C is 21 mm.]* *(Delhi H.S. 1964)*

5. 2·943 gm. of metal was treated with excess of an acid. The volume of hydrogen collected over water at 15°C and 752·5 mm. pressure was found to be 1083·6 c.c. Calculate the equivalent weight of the metal. *[Aq. tension at 15°C was 12·5 mm. ; weight of one c.c. of hydrogen at N.T.P. was 0·00009 gm.]* *(Delhi H.S. 1961)*

6. 5 gm. of an acid was diluted with water and treated with excess of zinc. Hydrogen liberated weighed 0·0667 gm. Calculate the equivalent weight of the acid. How much sodium hydroxide will be needed to neutralize 9 gm. of the acid ? *(Delhi H.S. 1966)*

7. What is the equivalent weight of a metal, 24 gm. of which evolve from an acid 22·4 litres of hydrogen at N.T.P. ? *(U.P. Board Inter. 1967)*

Oxide Formation Method

8. On heating 0·8567 gm. of copper oxide in a current of hydrogen the resulting copper weighed 0·6842 gm. What is the equivalent weight of copper ? *(I.I.T. Admission Test 196)*

9. 1·62 gm. of zinc when dissolved in nitric acid gave zinc nitrate. The nitrate when strongly heated left a residue of zinc oxide which accurately weighed 2·02 gm. Find the equivalent weight of zinc. *(I.I.T. Admission Test 196)*

10. Carbon dioxide produced by burning 2·6 gm. carbon in oxygen was absorbed in weighed soda-lime. Increase in weight of soda-lime was 9·7 gm. Calculate the equivalent weight of carbon. *(Senior Cambridge 1965 Dec.)*

Chloride Formation Method

11. 0·54 gm. of silver, dissolved in nitric acid, gave on addition of a solution of common salt 0·7175 gm. of silver chloride. Determine the equivalent weight of silver.

Metal Displacement Method

12. 1·201 gm. of zinc gave 1·497 gm. of zinc oxide on treatment with nitric acid and subsequent ignition. In a second experiment 0·543 gm. of zinc precipitated 0·527 gm. of copper from copper sulphate solution. Calculate the equivalent weights of copper and zinc, assuming that of oxgen to be 8.

Electrolytic Method :

13. [illegible]

14. Equal quantities of electricity displaced 2·158 gm. silver and 1·314 gm. of another metal. Calculate the equivalent weight of the metal that of silver being 107·9. *(Delhi H.S. 1966)*

15. How much copper and silver will be displaced by an electric current which displaced 5·6 litres of hydrogen at N.T.P. ? *(Senior Cambridge 1962 July)*

Double Decomposition Method

16. 0·194 gm. of a metallic chloride on treatment with excess of silver nitrate gave a precipitate of 0·5 gm. silver chloride. Calculate the equivalent weight of the metal. *(U.P. Board Inter. 1964)*

17. 1·05 gm. of metallic carbonate left on ignition 0·5 gm. of oxide. Calculate the equivalent weight of metal. *(Travancore Inter. 1964)*

18. [illegible] solution [illegible] ited silver [illegible] ulate the [illegible] *niv. 1961)*

Test Your Understanding

19. Fill in the blanks in the following :

(i) 0·5 g. of a metal liberated 112 c.c. of hydrogen at N.T.P. Its eq. wt.=....

(ii) 0·4 g. of a metal gave 0·5 g. oxide. Its eq. wt.=......

(iii) 0·108 g. metal gave 0·1435 g. chloride. Its eq. wt.=......

(iv) 0·6 g. magnesium displaced 1·59 g. copper. Eq. wt. of Mg=12 and that of copper=.. ...

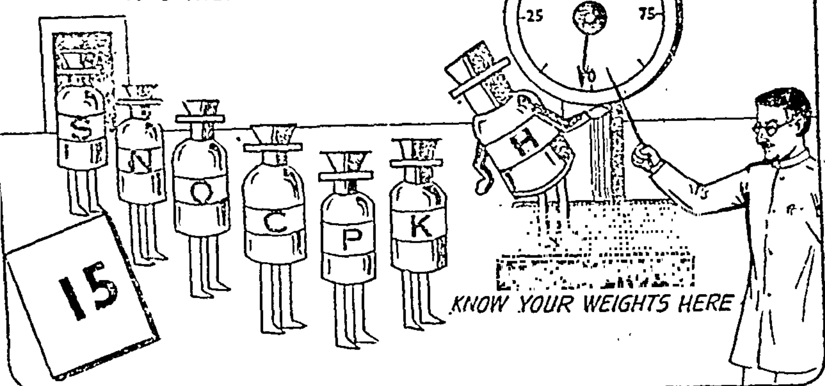
(v) 1 gm. of a metal carbonate gave on heating 0·56 gm. of the metal oxide. Eq. wt. of metal=... ..

KEY

(i) 50 ; (ii) 32 ; (iii) 108 ; (iv) 31·8 ; (v) 20.

ANSWERS

3. 32·71	4. 32·57	5. 32·96
6. 72·26 ; 4·996 gm.	7. 12	8. 31·74
9. 32·4	10. 2·93	11. 108
12. 31·50 ; 32·45	13. 31·90	14. 65·7
15. Cu=15·8 gm. ; Ag=54 gm.		16. 20·18
17. 12	18. 23·07.	



Atomic Weights

1. **Weight of an Atom.**—Atoms are too light particles to be weighed by any laboratory balance. Weight of a carbon atom has been found by calculation to be 0·000,000,000,000,000,000,000,019,79 gram ($=1·979 \times 10^{-23}$ gm.), an exceedingly small weight with no practical meaning. This shows that gram is too big a unit to weigh an atom and to express the weight of an atom in grams is as ridiculous as to express the weight of a grain of sand in tons.

The difficult situation was solved by selecting the weight of one-twelfth of carbon atom as standard and termed as atomic mass unit (amu). It was assigned the weight of 12 amu to have the relative weight of the lightest element, hydrogen, as 1 amu.

2. **Atomic Weight.**—The relative weight of an atom as compared with carbon is called its atomic weight. It does not tell how much an atom actually weighs. It is defined as follows :

Atomic weight of an element is the "average relative" weight of its atoms compared with that of carbon atom (C^{12}*-isotope*) *taken as 12 amu.*

Different isotopes of the same element have different weights. Atomic weight is the "*average*" of their individual relative weights. The word "*relative*" used along with "*average*" in the definition is to indicate that *atomic weight is only a number.*

3. **Atomic Weights Related to Equivalent Weights.**—Let A, E and v be the at. wt., eq. wt. and valency of an element respectively. From the definition of valency, we know that :

v atoms of hydrogen combine with one atom (At. wt.$=A$) of the element, *i.e.*, v parts by weight of hydrogen combine with A parts by weight of the element.

Or 1 part by weight of hydrogen combines with A/v parts by weight of element. This is, by definition, the equivalent weight $(=E)$ of the element.

$$\therefore \quad E = A/v$$

$$\text{or} \quad A = E \times v$$

i.e., Atomic Weight=Equivalent weight×Valency.

4. **Determination of Atomic Weights.**—Equivalent weight of an element can be easily and accurately determined by different methods discussed in the last chapter. So the problem of determination of atomic weights reduces to the determination of valency. Product of equivalent weight and valency gives the atomic weight. Different methods employed for the determination of weights are :

(1) **Cannizzaro's Method.** Since atom is an indivisible particle, no molecule of a compound can have less than one atom of any of its elements. Thus *atomic weight may be defined as the smallest weight of the element contained in one molecule of any of its compounds.* Based on this definition, Cannizzaro's method for determination of atomic weights involves the following steps :



Theodore William Richard
(1869—1928)
An American chemist ; who was awarded Nobel Prize for Chemistry in 1914. He did remarkable work on the determination of atomic weight.



S Cannizzaro
(1826—1910)
Italian chemist He was the first (in 1854) to realise the importance of Avogadro's work in connection with atomic weight

(i) Determination of the molecular weights of large number of compounds, *all containing the given element.*

(ii) Determination of the percentage of the given element in each of the compounds chosen above.

(iii) Calculation of the weight of the given element *in one molecule* of each compound.

Example 3. *The oxide of an element contains 33·33% of the element. The same forms a chloride whose vapour density is 59·25. Calculate the equivalent weight, atomic weight and valency of the element.*

Percentage of element $= 33.33$

" " oxygen $= 100 - 33.33 = 66.67$

Eq. wt. of the elment $= \frac{33.33}{66.67} \times 8 = 4.$

Let the valency of the element be x.

At. wt. of the element $=$ Eq. wt. $\times$ valency $= 4x$.

Formula of its chloride will be MCl_x with ml. wt.

$= 4x + 35.5x = 39.5x$



Eilhardt Mitscherlich (1794—1863)

German chemist; studied chemistry under Berzelius. He was famous for his researches on crystalline structure and discovered isomorphism in 1819.

Vapour density of the chloride (*given*)

$= 59.25$

$\therefore$ Mol. wt. of the chloride

$= 59.25 \times 2 = 118.5$

Equating this to the molecular weight calculated from the formula, we have

$39.5x = 118.5$

or $x = \frac{118.5}{39.5} = 3$

$\therefore$ **Valency of the element = 3.**

Atomic weight = Eq. wt. $\times$ valency

$= 4 \times 3 = 12.$

(4) By Mitscherlich's Law of Isomorphism (1820). *Substances crystallizing in the same crystalline form are called* isomorphous. Mitscherlich was the first to recognize that the structure of a crystal is in some way related to its chemical composition. He put forward his well-known law of isomorphism which states: *Isomorphous substances possess similar chemical constitution, i.e., they contain same total number of atoms similarly arranged.* For example, ferrous sulphate ($FeSO_4.7H_2O$) and zinc sulphate ($ZnSO_4.7H_2O$) are isomorphous. Some other examples are :

(*i*) Potassium sulphate (K_2SO_4) and potassium chromate (K_2CrO_4).

(*ii*) Sodium phosphate (Na_3PO_4) and sodium arsenate (Na_3AsO_4).

Characteristics of isomorphous compounds are :

(*a*) They possess similar crystalline structures.

(*b*) Mixed crystals are obtained when a mixture of their solutions is concentrated and crystallized.

(*c*) A crystal of one can grow when placed in a saturated solution of the other.

(*d*) In isomorphous compounds, weight of two elements, which combine with the same combined weight of the other elements, are in the ratio of their atomic weights.

Utility of the law of isomorphism in the determination of atomic weights is illustrated by the solved examples given below :

Example 4. *The sulphate of a metal contain 20'9% of the metal and is isomorphous with* $ZnSO_4.7H_2O$. *What is the probable atomic weight of the metal ?*

The sulphate being isomorphous with $ZnSO_4.7H_2O$, its molecular formula must be $MSO_4.7H_2O$. Here M is the given metal of atomic weight, say x.

Mol. wt. of the sulphate$=x+96+7\times18$

$=x+222$

Percentage of the metal in the sulphate

$$=\frac{x}{x+222}\times100=20{\cdot}9 \quad \text{....(Given)}$$

or $100x=20{\cdot}9x+20{\cdot}9\times222$

or $100x-20{\cdot}9x=20{\cdot}9\times222$

or $79{\cdot}1x=20{\cdot}9\times222$

whence $x=\frac{20{\cdot}9\times222}{79{\cdot}1}=58{\cdot}65.$

∴ **Probable at. wt. of the metal=58'65.**

Example 5. *Magnesium sulphate contains 9'75% of Mg and 39'02% of* [illegible] *of* SO_4. [illegible] *Mg. The* [illegible]

Percentage of magnesium in magnesium sulphate=9'75

i.e., 9'75 parts by weight of magnesium combine with (100−9'75=90'25) parts by weight of other elements combined...(1)

Percentage of zinc in zinc sulphate=22'6.

i.e., 22'6 parts by weight of zinc combine with (100−22'6 =77'4) parts by weight of other elements combined.

∴ Wt. of zinc which combines with 90'25 parts of other

$$\text{elements}=\frac{22{\cdot}6}{77{\cdot}4}\times90{\cdot}25=26{\cdot}35 \quad ...(2)$$

Now from (1) and (2) weights of magnesium and zinc which combine with the same combined weight of the other elements are 9'75 *and* 26'35 *respectively. These must be in* the ratio of their atomic weights as the two sulphates are isomorphous, *i.e.,*

$$\frac{9{\cdot}75}{26{\cdot}35}=\frac{\text{At. wt. of Mg}}{\text{At. wt. of Zn}}=\frac{x}{65}$$

whence $x=\frac{9{\cdot}75\times65}{26{\cdot}35}=24{\cdot}05.$

∴ At. wt. of Mg=24'05.

QUESTIONS AND PROBLEMS

Essay-type Questions

1. (a) Define the terms (i) Equivalent weight, (ii) Atomic weight, and (iii) Valency. How are these related to one another ?
(Haryana H.S. 1970 ; All India 1968 ; Delhi 1963, 61 ; Punjab Pre-Univ. 1969)

(b) Which of the following should necessarily be whole numbers ?
Atomic weight, Atomic number, Equivalent weight and Valency.
(I.I.T. Admission Test 1971)

2. State Dulong and Petit's law and discuss its importance in the determination of atomic weights. *(Punjab & Nagpur Pre. Univ. 1971 ; Delhi H.S. 1960 ; Bombay Inter. 1963 Supp., 61).*

3. Write the informative notes on "Law of Isomorphism" and atomic heat of an element. *(Bombay Inter. 1963 Supp., 63)*

4. What is the Mitscherlich's Law of Isomorphism ? Explain clearly its value in the determination of atomic weights. *(Bombay Inter. 1962)*

5. What are the methods by which the atomic weight of the element can be determine ?

Cannizzaro's Method

6. The following compounds of nitrogen were analysed and their vapour densities determined. The data obtained are tabulated below :

Name of Compound	V.D.	% of Nitrogen
1. *Nitrous oxide*	22	63·6
2. *Nitric oxide*	15	46·7
3. *Nitrogen dioxide*	23	30·4
4. *Cyanogen*	26	53·8
5. *Ammonia*	8·5	82·4

From the above data, calculate the approximate atomic weight of nitrogen.

7. Phosphorus combines with oxygen, hydrogen, chlorine and fluorine to give compounds containing 56·36, 91·17, 22·54 and 35·22 per cent of phosphorus respectively. The vapour densities of the compounds (H=1) are 110, 17, 68·95 and 44 respectively. From the data deduce the atomic weight of phosphorus.

At. Wt.=Eq. Wt.×Valency (Given directly)

8. Valency of a metal is 3 and there is 31·6% oxygen in its oxide. Calculate the atomic weight of the metal. *(Senior Cambridge 1965)*

9. 1·5 gm. of a divalent metal displaced 4·0 gm. of copper from copper sulphate solution. Calculate the equivalent weight and atomic weight of the metal. [*Cu*=64] *(Senior Cambridge 1962 Nov.)*

Dulong and Petit's Rule

10. Specific heat of a divalent metal is 0·1. Calculate its approximate equivalent weight. *(Senior Cambridge 1964)*

11. Specific heat of an element is 0·031 calorie per gram per degree. 25·9 gm. of this element combines with 4 gm. oxygen. Calculate the atomic weight of the element. *(I.I.T. Admission Test 1966)*

12. Specific heat of a metal is 0·25. What will be its approximate atomic weight ? The equivalent weight of the metal is 9, find out its valency. *(Senior Cambridge 1963 Dec.)*

13. 1·05 gm. of a metal on oxidation gave 1·50 gm. of oxide. Specific heat of the metal was found to be 0·1138. Calculate its atomic weight.
(*Bihar H.S. 1961*)

14. 1·217 gm. of a metal chloride on heating with concentrated sulphuric acid gave 1·327 gm. of the sulphate. If specific heat of the metal be 0·0314, calculate its atomic weight. (*Bihar H.S. 1963 Supp.*)

15. On passing 0·125 ampere current through a metallic salt solution for 20 minutes, 0·1667 gm. of metal was deposited. Specific heat of the metal is 0·0556 calorie per gm. per degree. Calculate its atomic weight.
(*I.I.T. Admission Test 1963*)

16. The bromide of a metal contains 81·08 per cent bromine. The specific heat of the metal is 0·11. Calculate the equivalent weight, atomic weight and the valency of the metal. (*U.P. Board Inter. 1965*)

17. 1·0 gm. of a metal yielded 1·328 gm. of its chloride. The specific heat of the metal is 0·059. Calculate the atomic weight of the metal.
(*Punjab H.S. 1964*)

18. [illegible]

19. 0·45 gm. of a metal when treated with excess of dilute sulphuric acid gave 176·6 c.c. of moist hydrogen measured at 23°C and 743 mm pressure. The specific heat of the metal is 0·091. Calculate its accurate atomic weight. [*Aqueous tension at 23°C=21 mm.*] (*Delhi H.S. 1964*)

From Vapour Density of Chloride

20. The chloride of a metal contains 80 per cent of chlorine. If the vapour density of the chloride in vapour state be 66·56, calculate the atomic weight of the metal and write down the formula of the chloride putting *M* for the metal. (*U.P. Board Inter. 1967*)

21. The oxide of an element contains 66·67% oxygen. It forms a chloride whose vapour density is 79. Calculate the atomic weight of the metal.
(*Haryana Board H.S. 1970*)

22. A known metal forms two chlorides containing 50·91% and 46·37% of the metal respectively. Calculate the atomic weight of the metal.

Note. *Maximum atomic weight of any known element is approximately 260.*
(*I.I.T. Admission Test 1965*)

Law of Isomorphism

23. 1 gm. of the chloride of a metal when treated with excess of silver nitrate produced 0·965 gm. of dry AgCl. Calculate the atomic weight of the metal, given that it closely resembles barium in its properties.

24. Potassium sulphate (K_2SO_4) is isomorphous with potassium selenate. The composition of potassium selenate is K=35·29% ; Se=35·75% ; O=28·96%. Calculate the atomic weight of selenium. (*All India H.S. 1969*)

25. A metal *M* forms a sulphate which is isomorphous with magnesium sulphate, $MgSO_4.7H_2O$. Calculate the atomic weight of the metal *M* when 0·6538 gm. of the metal *M* displaces 2·16 gm. of silver from nitrate solution.

26. An element *A* forms a chloride which contains 29·34% by weight of chlorine and is isomorphous with potassium chloride. Calculate the atomic weight of *A*. (*Delhi Pre-Medical 1962*)

Test Your Understanding

27. Fill in the blanks in the following :
   (i) According to......the product of......and......of a solid=6·4.
   (ii) Atomic weight = Equivalent weight × ......
   (iii) Specific heat of a divalent element is 0·27, its approximate equivalent weight=......
   (iv) Substances possessing similar crystalline forms are called......
   (v) Eq. wt. of an element is 10·33 and the vapour density of its chloride is 68·75. Its at. wt.=......

28. (a) What is the valency of an element of which equivalent weight is 12 and the specific heat is 0·25 ? *(I.I.T. Admission Test 1971)*

(b) The specific heat of the metal is 0·057. Its equivalent weight is 37·8. What is the correct atomic weight ? *(Nagpur Pre-Univ. 1971)*

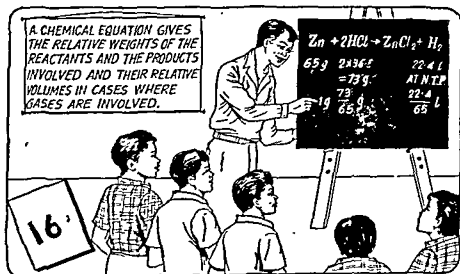
KEY

27. (i) Dulong and Petit, atomic weight, specific heat ; (ii) valency (iii) 11·85 ; (iv) isomorphous ; (v) 31.

28. (a) 2 ; (b) 113·4.

ANSWERS

6. 14	7. 31	8. 52
9. 12 ; 24	10. 32	11. 207·2
12. 25·6 ; 3	13. 56	14. 205
15. 107·9	16. 18·67 ; 56·01	17. 108·2
18. 59	19. 65·22	20. 26·625 ; MCl_3
21. 16	22. 184	23. 226·4
24. 79·03	25. 65·38	26. 85·49.



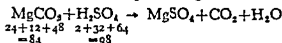
Chemical Arithmetic

1. Problems Based on Equations.—According to the modern atomic theory, atoms possess a definite weight and no atoms are lost or gained during a chemical reaction. It follows, therefore, that the relative weights of the reactants and the products of a chemical reaction, can be calculated from its equation. Different types of problems pertaining to chemical reactions are :

TYPE I. Based on Weight-Weight relationship.

Example 1. *What weight of sulphuric acid will be required to completely dissolve 3 gm. of magnesium carbonate ?*

The chemical equation representing the reactions is :



$$\underset{\substack{24+12+48\\=84}}{MgCO_3} + \underset{\substack{2+32+64\\=98}}{H_2SO_4} \rightarrow MgSO_4 + CO_2 + H_2O$$

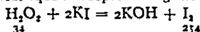
84 gm. of $MgCO_3$ require 98 gm. of H_2SO_4 for complete dissolution.

3 gm. of $MgCO_3$ will require $\frac{98}{84} \times 3 = 3{\cdot}5$ gm. of H_2SO_4 for complete dissolution.

Sulphuric acid required=3·5 gm.

Example 2. *10 c.c. of a solution of hydrogen peroxide liberated 0·5 gm. of iodine from a solution of potassium iodide. Calculate the percentage of hydrogen peroxide in the solution.*

The chemical equation representing the chemical reaction is :



$$\underset{34}{H_2O_2} + 2KI = 2KOH + \underset{254}{I_2}$$

From the equation it is clear that 254 gm. of iodine are liberated from the potassium iodide by 34 gm. of hydrogen peroxide.

∴ 0·5 gm. of iodine will be liberated from a solution of potassium iodide by $\frac{34}{254} \times 0{\cdot}5 = 0{\cdot}067$ gm. of hydrogen peroxide.

Wt. of hydrogen peroxide present in 10 c.c. = 0·067 gm.

" " " " 100 c.c. = 0·67 gm.

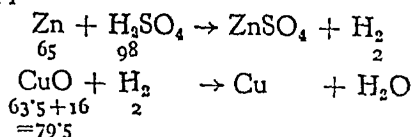
∴ Percentage of hydrogen peroxide in the solution = 0·6'

Type II. Based on reactions taking place in successio

In certain cases two or more chemical reactions are involve in such a way that one of the products in the first reaction reac again in the second reaction. In such cases separate calculations fc each step are not required. A one-step calculation is always poss ble as illustrated in the few examples given below :

Example 3. *What weight of zinc and sulphuric acid woul be required to produce enough hydrogen to reduce completely 8·5 gr of copper oxide to copper ?*

The chemical equations for production of hydrogen and re duction of copper oxide are :



$$\underset{65}{Zn} + \underset{98}{H_2SO_4} \rightarrow ZnSO_4 + \underset{2}{H_2}$$

$$\underset{\substack{63{\cdot}5+16\\=79{\cdot}5}}{CuO} + \underset{2}{H_2} \rightarrow Cu + H_2O$$

From the equation it is clear that 65 gm. of zinc and 98 gn of sulphuric acid are required to produce enough hydroge (=2 gm.) to reduce completely 79·5 gm. of copper oxide to coppe

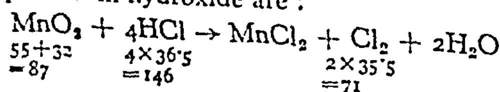
Their weights required for reducing 8·5 gm. copper oxide t copper, will be :

$$\text{Zinc} = \frac{65}{79{\cdot}5} \times 8{\cdot}5 = 6{\cdot}95 \text{ gm.}$$

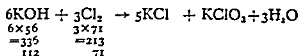
$$\text{Sulphuric acid} = \frac{98}{79{\cdot}5} \times 8{\cdot}5 = 10{\cdot}47 \text{ gm.}$$

Example 4. *How much manganese dioxide and how muc hydrochloric acid (33·% HCl) will be required to furnish chlorin necessary to convert 40 gm. of potassium hydroxide completely int chlorate and chloride ?*

The chemical equations for preparation of chlorine and it reaction with potassium hydroxide are :



$$\underset{\substack{55+32\\=87}}{MnO_2} + \underset{\substack{4\times36{\cdot}5\\=146}}{4HCl} \rightarrow MnCl_2 + \underset{\substack{2\times35{\cdot}5\\=71}}{Cl_2} + 2H_2O$$



$$6KOH + 3Cl_2 \rightarrow 5KCl + KClO_3 + 3H_2O$$
$6 \times 56 = 336$, $3 \times 71 = 213$
or 112, 71

From the equations it is clear that 112 gm. of KOH need 71 gm. of chlorine which is further obtained from 87 gm. of MnO_2 and 146 gm. of HCl.

$\therefore$ MnO_2 required for 40 gm. of $KOH = \frac{87}{112} \times 40$

$= 31·07$ gm.

Similarly HCl „ „ „ $= \frac{146}{112} \times 40$ gm.

But the given sample contains 33% HCl.

Hence wt. of the given HCl required

$$= \frac{146}{112} \times 40 \times \frac{100}{33} = 158·01 \text{ gm.}$$

TYPE III. Based on Weight-Volume relationship.

Here we come across problems wherein weights are given and volumes are required or the converse. In solving these we have to keep in mind the fact that *one gram mole of any gas at N.T.P. occupies 22·4 litres.*

Exercise 5. *A large lamp of zinc is placed in 100 gm. of a solution of HCl. 150 ml. of hydrogen at 15°C and 740 mm. pressure are evolved. Calculate the percentage of HCl in the solution.*

Wt. of HCl solution $= 100$ gm.

Vol. of hydrogen evolved $= 150$ ml. at 15°C and 740 mm.

Let us calculate its volume of hydrogen at N.T.P.

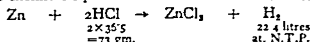
$V_1 = 150$ ml. $\quad V_2 = ?$

$P_1 = 740$ mm. $\quad P_2 = 760$ mm.

$T_1 = 15 + 273 = 288°$ Abs. $\quad T_2 = 273°$ Abs.

$$\therefore V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{740 \times 150 \times 273}{288 \times 760} = 138·5 \text{ ml.}$$

The chemical equation for the reaction involved is



$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$
$2 \times 36·5 = 73$ gm. ; 22·4 litres at. N.T.P.

From the equation it is clear that 22,400 ml. of hydrogen at N.T.P. are liberated by HCl = 73 gm.

$\therefore$ Wt. of HCl needed for liberating 138·5 ml. of H_2 at

$$\text{N.T.P.} = \frac{73}{22{,}400} \times 138·5 = 0·451 \text{ gm.}$$

Now 0·451 gm. HCl is present in 100 gm. of the solution.

$\therefore$ Percentage of HCl in the solution $= 0·451$.

Example 6. *In a certain experiment 10 litres of carbon dioxide at 27°C and 765 mm. pressure are required. How much marble of 96·5% purity would be required to prepare the above quantity of the gas under the experimental conditions?*

Volume of carbon dioxide at N.T.P.

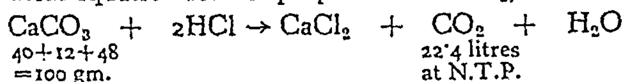
$V_1 = 10$ litres. $V_2 = ?$

$P_1 = 765$ mm. $P_2 = 760$ mm.

$T_1 = 27 + 273 = 300°$ Abs. $T_2 = 273°$ Abs.

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{765 \times 10 \times 273}{300 \times 760} = 9·162 \text{ litres.}$$

Chemical equation for the preparation of CO_2, from marble is



$$\underset{\substack{40+12+48 \\ =100 \text{ gm.}}}{CaCO_3} + 2HCl \rightarrow CaCl_2 + \underset{\substack{22·4 \text{ litres} \\ \text{at N.T.P.}}}{CO_2} + H_2O$$

From the equation it is clear that 22·4 litres of CO_2 at N.T.P. are liberated from 100 gm. of marble.

∴ Wt. of marble required for liberating 9·162 litres of CO_2 at

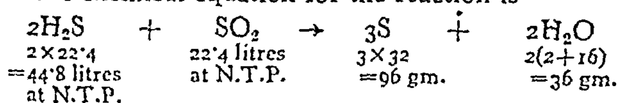
$$\text{N.T.P.} = \frac{100}{22·4} \times 9·162 \text{ gm.}$$

$$\text{Wt. of marble of 96·5\% purity needed} = \frac{100}{22·4} \times 9·162 \times \frac{100}{96·5}$$

$$= 42·39 \text{ gm.}$$

Example 7. *One litre of sulphur dioxide is mixed with one litre of hydrogen sulphide, both at N.T.P. Calculate the weight of each substance after the reaction.*

The chemical equation for the reaction is



$$\underset{\substack{2 \times 22·4 \\ =44·8 \text{ litres} \\ \text{at N.T.P.}}}{2H_2S} + \underset{\substack{22·4 \text{ litres} \\ \text{at N.T.P.}}}{SO_2} \rightarrow \underset{\substack{3 \times 32 \\ =96 \text{ gm.}}}{3S} + \underset{\substack{2(2+16) \\ =36 \text{ gm.}}}{2H_2O}$$

According to the above equation, 44·8 litres of H_2S at N.T.P. react with 22·4 litres of SO_2 at N.T.P. to produce 96 gm. of sulphur and 36 gm. of water.

∴ 1 litre of H_2S will react with half a litre of SO_2 to produce

$$\text{Sulphur} = \frac{96}{44·8} = 2·143 \text{ gm.}$$

$$\text{Water} = \frac{36}{44·8} = 0·803 \text{ gm.}$$

$$\text{Weight of half a litre of } SO_2 \text{ left unreacted} = \frac{64}{22·4 \times 2}$$

$$= 1·43 \text{ gm.}$$

Example 8. *A naturally-occurring mineral was found to contain (i) 42% $MgCO_3$; (ii) 55% $CaCO_3$ and the rest was*

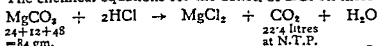
impurity. What volume of CO_2 measured at 15°C and 745 mm. pressure will be evolved by heating 10 gm. of the mineral with hydrochloric acid?

Wt. of mineral = 10 gm.

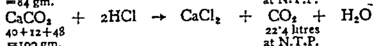
Wt. of $MgCO_3$ (42% in the mineral) = 4·2 gm.

,, $CaCO_3$ (55% in the mineral) = 5·5 gm.

The chemical equations for the action of HCl on these are :



$$\underset{\substack{24+12+48\\=84\text{ gm.}}}{MgCO_3} + 2HCl \rightarrow MgCl_2 + \underset{\substack{22\cdot4\text{ litres}\\\text{at N.T.P.}}}{CO_2} + H_2O$$



$$\underset{\substack{40+12+48\\=100\text{ gm.}}}{CaCO_3} + 2HCl \rightarrow CaCl_2 + \underset{\substack{22\cdot4\text{ litres}\\\text{at N.T.P.}}}{CO_2} + H_2O$$

84 gm. of $MgCO_3$ liberate 22·4 litres of CO_2 at N.T.P.

∴ 4·2 ,, ,, will liberate $= \frac{22\cdot4}{84} \times 4\cdot2$

$= 1\cdot12$ litres of CO_2 at N.T.P.

100 gm. of $CaCO_3$ liberate 22·4 litres of CO_2 at N.T.P.

5·5 gm. of $CaCO_3$ will liberate $= \frac{22\cdot4 \times 5\cdot5}{100}$

$= 1\cdot232$ litres of CO_2 at N.T.P.

Total CO_2 evolved $= 1\cdot12 + 1\cdot232 = 2\cdot352$ litres at N.T.P.

Vol. at 15°C and 745 mm. pressure $= \frac{760 \times 2\cdot352 \times 288}{273 \times 745}$

$= 2\cdot531$ litres.

TYPE IV. Based on Volume-Volume Relationship.

Examples based on volume-volume relationship have been separately given at length in Chapter 17—EUDIOMETRY.

TYPE V. Analysis of Mixtures.

Example 9. *A mixture of cuprous oxide and cupric oxide was found to contain 88% of copper. Using 64 as the atomic weight of copper, calculate the percentage of the two compounds of the mixture.*

Percentage of copper in cuprous oxide (Cu_2O)

$$= \frac{2 \times 64}{2 \times 64 + 16} \times 100 = \frac{128}{144} \times 100 = 88\cdot89$$

Percentage of copper in cupric oxide (CuO)

$$= \frac{64}{64+16} \times 100 = \frac{64}{80} \times 100 = 80.$$

We find that if w...

the percentage of copp

of cuprous oxide, the p

Thus the percentage of cuprous oxide in the mixture increases from 0 to 100 as the percentage of copper rises from 80 to 88·89, i.e., passes through an entire range of 88·89 − 80 = 8·89

But the actual percentage of copper is 88, *i.e.*, 88−80=8% in excess of the lower value.

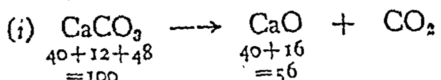
∴ Percentage of cuprous oxide in the mixture

$$=\frac{8}{8\cdot89}\times100=90.$$

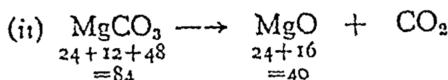
and Percentage of cupric oxide=100−90=10.

Example 10. *You are given a mixture of calcium and magnesium carbonates. 1·84 gm. of the mixture are ignited until no further loss of weight takes place. The residue weighs 0·96 gm. What is the percentage composition of the mixture ?*

Chemical equations for the ignition of carbonates are :



(*i*) $\underset{\substack{40+12+48\\=100}}{CaCO_3} \longrightarrow \underset{\substack{40+16\\=56}}{CaO} + CO_2$



(ii) $\underset{\substack{24+12+48\\=84}}{MgCO_3} \longrightarrow \underset{\substack{24+16\\=40}}{MgO} + CO_2$

We find that if the mixture were wholly made up of $CaCO_3$, the weight of the residue from 1·84 gm. would have been

$$1\cdot84\times\frac{56}{100}=1\cdot03 \text{ gm.}$$

On the other hand, if it were wholly made up of $MgCO_3$, the weight of the residue would have been $1\cdot84\times\frac{40}{84}=0\cdot8762$ gm.

Hence the percentage of $CaCO_3$ in the mixture increases from 0 to 100 as the weight of the residue increases from 0·8762 to 1·03 gm., *i.e.*, passes through an entire range of (1·03−0·8762).

=0·1538 gm.

But the residue left actually is only 0·96 gm., *i.e.*,

0·96−0·8762=0·0838 gm. in excess of the lower value.

Hence, percentage of $CaCO_3$ in the mixture$=\frac{0\cdot0838}{0\cdot1538}\times100$

=54·48

and percentage of $MgCO_3$ (*by difference*)=100−54·48=45·52.

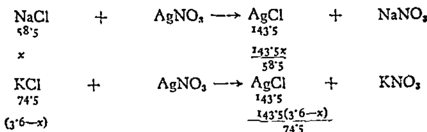
An alternative method for doing such problems is given in Example 11.

Example 11. *3·6 gm. of a mixture of sodium and potassium chlorides gave with silver nitrate 7·74 gm. of silver chloride. What was the percentage of each salt in the mixture ?*

Let the weight of sodium chloride in the mixture be *x* gm.

Then weight of potassium chloride=(3·6−*x*) gm.

Chemical equations for the action of silver nitrate on these chlorides are :



$$\underset{\substack{58\cdot5\\x}}{NaCl} + AgNO_3 \longrightarrow \underset{\substack{143\cdot5\\ \frac{143\cdot5x}{58\cdot5}}}{AgCl} + NaNO_3$$

$$\underset{\substack{74\cdot5\\(3\cdot6-x)}}{KCl} + AgNO_3 \longrightarrow \underset{\substack{143\cdot5\\ \frac{143\cdot5(3\cdot6-x)}{74\cdot5}}}{AgCl} + KNO_3$$

58·5 gm. of NaCl yield 143·5 gm. of AgCl.

$\therefore$ x gm. of NaCl yield$=\frac{143\cdot5x}{58\cdot5}$gm.

Again 74·5 gm. of KCl yield 143·5 gm. of AgCl.

$\therefore$ $(3\cdot6-x)$ *gm. of* KCl *will yield* AgCl$=\frac{143\cdot5(3\cdot6-x)}{74\cdot5}$ gm.

Total wt. of AgCl obtained$=\frac{143\cdot5x}{58\cdot5}+\frac{143\cdot5(3\cdot6-x)}{74\cdot5}=7\cdot74$

or $2\cdot452x+1\cdot926(3\cdot6-x)=7\cdot74$

or $2\cdot452x-1\cdot926x=7\cdot74-6\cdot933$

or $0\cdot526x=0\cdot807$ whence $x=1\cdot534$

$\therefore$ Percentage of NaCl$=\frac{1\cdot534}{3\cdot6}\times100=42\cdot62$

and Percentage of KCl$=100-42\cdot62=57\cdot38$.

QUESTIONS AND PROBLEMS

Direct Weight Relationship

1. (*a*) How many moles of water should be electrolysed to produce 160 grams of oxygen ? (*Punjab Pre-University 1971*)

(*b*) What maximum weight of aluminium oxide could be obtained by heating 7·8 gm. pure aluminium hydroxide ? (*Senior Cambridge 1961 Dec.*)

2. 100 gm. of marble chips are dropped into 500 gm of a solution of hydrochloric acid containing one-tenth of its weight of the pure acid. How much of the chips will remain undissolved and what weight of anhydrous calcium chloride could be obtained from the solution ?
(*Delhi Pre-University 1960*)

3. What minimum weight of water is needed to slake 1 kgm. of quicklime, assuming no loss by evaporation ? (*Senior Cambridge 1966 July*)

4. The maximum weight of copper sulphate crystals, $CuSO_4.5H_2O$, obtainable from 20·0 gm. of a sample of brass containing only zinc and copper is 37·2 gm. What weight of zinc was present in the 20·0 gm of brass ?
(*Senior Cambridge 1966 July*)

5. Hydrogen reacts essentially completely with cupric oxide (CuO) to form copper and water. How many grams of hydrogen are needed to produce (*a*) 0·200 gram of copper, (*b*) 0·200 mole of copper, and (*c*) 0·290 gram of water ?
(*Delhi H.S. 1 3*)

Reactions taking place in Succession

6. What volume of solution of hydrochloric acid containing 73 grams per litre would suffice for the exact neutralization of the sodium hydroxide obtained by allowing 0·46 gram of metallic sodium to act upon water?

7. Hydrogen is generated by the action of steam on hot magnesium. Calculate the weight of magnesium that will be required to produce just sufficient hydrogen to combine with all the oxygen that can be obtained by the complete decomposition of 24·5 gm. potassium chlorate ($KClO_3$). *(Delhi H.S. 1966)*

Weight-Volume Relationship

8. What weight of iron would be required to liberate 10 litres of hydrogen at N.T.P. by reaction with dilute hydrochloric acid. *(Senior Cambridge 1966 July)*

9. 1·68 gram of a mixture of dry sodium carbonate and sodium bicarbonate containing 75% of the latter was heated until there was no more loss in weight. Calculate the volume of CO_2 evolved at N.T.P. *(Punjab Pre-University 1964)*

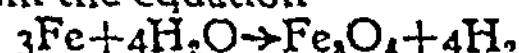
10. From the equation



$$C + 2H_2SO_4 \rightarrow CO_2 + 2H_2O + 2SO_2$$

Calculate: (*i*) the weight of carbon oxidised by the action of 19·6 gm. of sulphuric acid; and (*ii*) the volume of sulphur dioxide measured at N.T.P. liberated at the same time. *(Senior Cambridge 1964 Dec.)*

11. Calculate from the equation



$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

(*a*) the maximum volume of hydrogen measured at N.T.P. that could be obtained by using 56 gm. of iron, (*b*) the weight of black oxide of iron that would be formed at the same time. *(Senior Cambridge 1963 July)*

12. One gram of a mixture of sand and potassium chlorate gave on heating 224 c.c. of oxygen at N.T.P. Calculate the percentage of sand in the mixture. *(Punjab Pre-University 1963)*

13. Find out the volume of air at 91°C and 700 mm. pressure that would be required to completely burn one kilogram of coal containing 90% carbon and 10% incombustible matter. (Air contains 20% oxygen by volume.) *(Punjab Pre-Medical/Pre-Engg./B.Sc. I Year 1963)*

14. Chlorine reacts with a solution of magnesium bromide liberating bromine and forming chloride ions. If there be 3·68 gm. of magnesium bromide in a solution, what volume of chlorine measured at N.T.P. will react with it and what weight of bromine will be set free? (Mg=24, Cl=35·5, Br=80) *(Delhi H. S. 1968)*

15. Exactly 3 gm. of pure magnesite (magnesium carbonate) were treated with 5 gm. of dilute sulphuric acid. After all action had ceased, it was found that 0·48 gm. was left undissolved. Calculate the percentage strength of sulphuric acid. In this reaction what volume of carbon dioxide measured at 21°C and 72 cm. pressure would be evolved? *(Punjab Inter. 1962)*

16. Calculate the volume of dry CO_2 at 27°C and 75 cm. Hg pressure which will be required to dissolve 10 gm. of calcium carbonate suspended in water. *(Delhi H.S. 1969)*

17. How much potassium chlorate is needed to get enough oxygen for completely burning 84 litres of carbon monoxide at N.T.P.? *(Punjab Pre-University 1962)*

Analysis of Mixtures

18. 10 gm. of a mixture of anhydrous nitrates of two metals *A* and *B* were heated to a constant weight and gave 5·531 gm. of a mixture of the corresponding oxides. The equivalent weights of *A* and *B* are 103·6 and 31· respectively. What was the percentage of *A* in the mixture? *(Punjab Inter. 1966)*

19. One gm. of a mixture of $CaCO_3$ and $MgCO_3$ on treatment with dilute hydrochloric acid gave 254·9 ml. of carbon dioxide at 17°C and 750 mm. Calculate the composition of the mixture.
(Punjab Pre-Medical/Pre-Engg./B.Sc. I Year 1964)

20. 1·02 gm. of a mixture or $CaCO_3$ and $MgCO_3$ gives 246·4 c c. of CO_2 at N.T.P. Calculate the percentage composition of the mixture.
(Banaras Inter. 1964)

21. Equal weights of mercury and iodine are allowed to react completely to form a mixture of mercurous and mercuric iodides. Calculate the ratio of *the weights of mercurous and mercuric iodides formed.*
(I.I.T. Admission Test 1966)

22. 600 c.c of ozonised oxygen at N.T.P. were found to weigh 1 gm. Calculate the volume of ozone in the ozonised oxygen. *(Bombay Inter. 1962)*

ANSWERS

1. (*a*) 10 moles ; (*b*) 5·1 gm.
2. 1·728 gm. per gallon.
3. 321 gm.
4. 10·48 gm.
5. (*a*) 0·006299 gm. ; (*b*) 0·4 gm. ; (*c*) 0·0222 gm.
6. 10 c.c.
7. 14·4 gm.
8. 25 gm.
9. 168 c.c.
10. (i) 1·2 gm. ; (*ii*) 4·48 litres
11. (*a*) 29·9 litres ; (*b*) 77·3 gm.
12. 18 33.
13. 12,160 litres.
14. Cl_2=4·48 litres ; Br_2=3·2 gm.
15. 58 8% ; CO_2=763·8 c c.
16. 249·4 ml.
17. 153·125 gm.
18. 51·62%.
19. $CaCO_3$=70·03% ; $MgCO_3$=29·97%.
20. $CaCO_3$=58·82% ; $MgCO_3$=41·18%.
21. 53 : 74.
22. O_2=400 c.c. ; O_3=200 c.c.

BASIS OF EUDIOMETRIC CALCULATIONS

WEIGHT VOLUME RELATIONSHIP

22·4 l. at N.T.P. — 1 gm. MOL. Wt.

GAY LUSSAC'S LAW — AVOGADRO'S LAW

17

H_2 + Cl_2 ⟶ HCl HCl

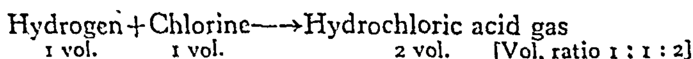
HYDROGEN 1 VOL. 1 MOL. — CHLORINE 1 VOL. 1 MOL. — HYDROGEN CHLORIDE 2 VOL. 2 MOL. — RATIO 1:1:2 1:1:2

VOL. RATIO = MOL. RATIO

Eudiometry

1. **Basis of Eudiometry.**—Eudiometry includes problems based on equations (volume-volume relationship). Gay Lussac's law and Avogadro's law constitute the basis of such calculations. In eudiometric calculations we make use of some important corollaries of Avogadro's law, *viz.*,

(i) The volume ratio *of various reactants and products in a gaseous reaction is also their* molecular ratio *and vice versa.* For example :



Hydrogen + Chlorine ⟶ Hydrochloric acid gas
1 vol.   1 vol.   2 vol.   [Vol. ratio 1 : 1 : 2]

Applying Avogadro's law :



n mol.   n mol.   2n mol.
or 1 mol.   1 mol.   2 mol. [Mol. ratio 1 : 1 : 2]

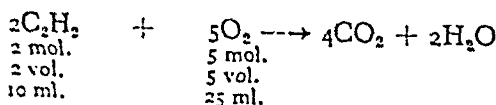
As given above the volume ratio as well as the molecular ratio of hydrogen, chlorine and hydrochloric acid gas in the above gaseous reaction is the same, *viz.*, 1 : 1 : 2.

(ii) *22·4 litres of any gas at N.T.P. weigh equal to one gram molecular weight and vice versa.* Different types of problems which we come across are given below :

TYPE I. Volume of gases taking part in a reaction.

Example 1. *What volume of oxygen at N.T.P. is required to effect complete combustion of 10 ml. acetylene ?*

Chemical equation for the complete combustion of acetylene is :



$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$$

$2C_2H_2$: 2 mol., 2 vol., 10 ml.

$5O_2$: 5 mol., 5 vol., 25 ml.

From the equation, it is clear that 2 vol. of acetylene requires 5 vol of oxygen for complete combustion.

∴ 10 ml. of acetylene at N.T.P. will require 25 ml. of oxygen at N.T.P. for complete combustion.

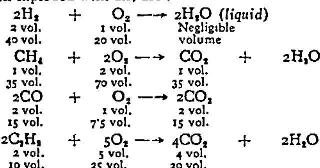
Example 2. *A sample of coal gas was found to contain 40% hydrogen, 35% methane, 15% carbon monoxide and 10% acetylene. 100 volumes of this gas were mixed with 600 volume of air (containing 21% of oxygen) in a eudiometer tube and exploded. Calculate the volume and composition of resulting mixture on cooling.*

100 volumes of coal gas contain 40% hydrogen(=40 volumes); 35% methane (=35 volumes) ; 15% carbon monoxide (=15 volumes) ; and 10% acetylene (=10 volumes).

Volume of oxygen present in 600 volumes of air (containing 21% oxygen)=6×21=126 volumes.

Volume of N_2 present=600−126=474 volumes.

Chemical equations for the combustion of these constituents when exploded with air, are :



$$\underset{\substack{2\text{ vol.}\\40\text{ vol.}}}{2H_2} + \underset{\substack{1\text{ vol.}\\20\text{ vol.}}}{O_2} \longrightarrow \underset{\substack{\text{Negligible}\\\text{volume}}}{2H_2O\ (liquid)}$$

$$\underset{\substack{1\text{ vol.}\\35\text{ vol.}}}{CH_4} + \underset{\substack{2\text{ vol.}\\70\text{ vol.}}}{2O_2} \longrightarrow \underset{\substack{1\text{ vol.}\\35\text{ vol.}}}{CO_2} + 2H_2O$$

$$\underset{\substack{2\text{ vol.}\\15\text{ vol.}}}{2CO} + \underset{\substack{1\text{ vol.}\\7·5\text{ vol.}}}{O_2} \longrightarrow \underset{\substack{2\text{ vol.}\\15\text{ vol.}}}{2CO_2}$$

$$\underset{\substack{2\text{ vol.}\\10\text{ vol.}}}{2C_2H_2} + \underset{\substack{5\text{ vol.}\\25\text{ vol.}}}{5O_2} \longrightarrow \underset{\substack{4\text{ vol.}\\20\text{ vol.}}}{4CO_2} + 2H_2O$$

As is evident from the equations above

Volume of oxygen used=20+70+7·5+25=122·5 vol.

Vol. of O_2 left unused =126−122·5 =3·5 vol.

Vol. of CO_2 produced =35+15+20 =70 vol.

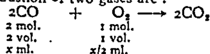
∴ The volume and composition of the resulting mixture on cooling is

Oxygen=3·5 vol. Nitrogen=474 vol.
Carbon dioxide=70 vol. Total volume=547·5 vol.

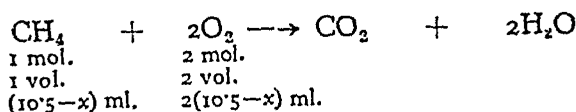
TYPE II. *Composition of Mixtures.*

Example 3. *Calculate the percentage composition by volume of a mixture of caron monoxide and methane, 10·5 ml. of which required 9 ml. of oxygen for complete combustion.*

Let the volume of CO in the mixture be x ml. Then vol. of methane will be $(105-x)$ ml. Chemical equations for the complete combustion of two gases are :



$$\underset{\substack{2\text{ mol.}\\2\text{ vol.}\\x\text{ ml.}}}{2CO} + \underset{\substack{1\text{ mol.}\\1\text{ vol.}\\x/2\text{ ml.}}}{O_2} \longrightarrow 2CO_2$$



CH_4	+	$2O_2$	$\longrightarrow$	CO_2	+	$2H_2O$
1 mol.		2 mol.				
1 vol.		2 vol.				
$(10·5-x)$ ml.		$2(10·5-x)$ ml.				

Volume of oxygen used up from the equations

$$=x/2+2(10·5-x)=21-1·5x \text{ ml.}$$

Equating this with the volume of O_2 actually used (=9 ml. as given in the data, we have

$21-1·5x=9$ or $1·5x=21-9=12$

whence $x=8$ ml. and $(10·5-x)=2·5$ ml.

∴ Percentage composition of the mixture is

$$\text{Carbon monoxide}=\frac{8}{10·5}\times 100=76·19\%$$

$$\text{Methane}=\frac{2·5}{10·5}\times 100=23·81\%$$

Example 4. *9·0 c.c. of a mixture of methane and ethylene were exploded with 30·0 c.c. (excess) of oxygen. After cooling the volume was 21·0 c.c. Further treatment with caustic potash solution reduced the volume to 7·0 c.c. Determine the composition of the mixture.*

Let the volume of methane (CH_4) be x c.c.

Then volume of ethylene (C_2H_4)$=(9-x)$ c.c.

Vol. of oxygen added $=30$ c.c.

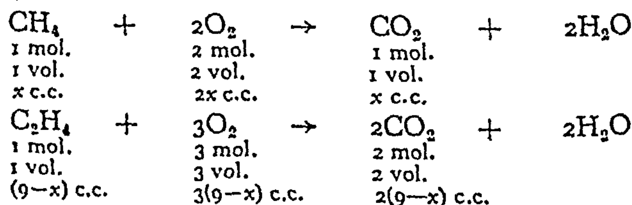
Vol. of mixture (CO_2+unused O_2) after combustion and cooling$=21$ c.c.

Vol. of unused oxygen left after treating the mixture with caustic potash which absorbs $CO_2=7$ c.c.

∴ Volume of CO_2 produced=Reduction in vol. with KOH$=21-7=14$ c.c.

and Vol. of O_2 used up $=30-7=23$ c.c.

Writing chemical equations for the combination of methane and ethylene, we have



CH_4	+	$2O_2$	$\rightarrow$	CO_2	+	$2H_2O$
1 mol.		2 mol.		1 mol.		
1 vol.		2 vol.		1 vol.		
x c.c.		$2x$ c.c.		x c.c.		
C_2H_4	+	$3O_2$	$\rightarrow$	$2CO_2$	+	$2H_2O$
1 mol.		3 mol.		2 mol.		
1 vol.		3 vol.		2 vol.		
$(9-x)$ c.c.		$3(9-x)$ c.c.		$2(9-x)$ c.c.		

Total CO_2 produced $x+2(9-x)$ $=$ 14 c.c.

(*From the Equations*) (*From the data*)

Or $x+18-2x=14$ or $18-x=14$

whence $x=18-14=4$ c.c.

∴ Composition of the mixture is :

Methane=4 c.c. and Ethylene$=9-4=5$ c.c.

TYPE III. Composition of a Gas.

Example 5. *50 vol. of a gas mixed with 70 vol. of O_2 give after explosion 50 vol. of CO_2, and after absorption by KOH 45 vol. of oxygen are left. What is the gas?*

Vol. of the gas taken	=50 vol.
,, ,, oxygen added	=70 vol.
,, ,, ,, left	=45 vol.
,, ,, ,, used up	=70−45=25 vol.
,, ,, CO_2 obtained	=50 vol.

Gas	+	O_2	→	CO_2
50 vol.		25 vol.		50 vol.
1 vol.		$\frac{1}{2}$ vol.		1 vol.
1 mol.		$\frac{1}{2}$ vol.		1 mol.
1 mol.		1 atom		1 mol.

From the data it is clear that 50 vol. of the gas combine with 25 vol. of oxygen to give 50 vol. of CO_2.

Or 1 vol. of the gas combines with $\frac{1}{2}$ vol. of oxygen to give 1 vol. of CO_2.

Or 1 mol. of the gas combines with $\frac{1}{2}$ mol. (*i.e.*, 1 atom) of oxygen to give 1 mol. of CO_2.

Or the gas contains one atom of oxygen less than CO_2, *i.e.*, it is

CO (Carbon monoxide).

TYPE IV. Molecular Formulae of Hydrocarbons from their combustion data.

A known volume of the hydrocarbon is exploded with excess of oxygen (known volume). The mixture obtained after explosion and cooling is carbon dioxide produced + oxygen unused. The mixture is treated with caustic potash (KOH) or caustic soda (NaOH) which absorbs the whole carbon dioxide present. *Thus decrease in volume with caustic potash is a measure of carbon dioxide produced and the residue left behind is unused oxygen.* From the combustion data the formula of the hydrocarbon can be calculated as illustrated by the solved examples given below:

Case (i). When the volume of oxygen added is known.

Example 6. *10 c.c. of a hydrocarbon mixed with 100 c.c. [illegible] ometer tube. The residual gas [illegible] c.c. of which 20 c.c. are absorb- [illegible] mainder by alkaline pyrogallol. Determine the formula of the hydrocarbon and name it.*

Vol. of hydrocarbon taken = 10 c.c.

Vol. of oxygen added = 100 c.c.

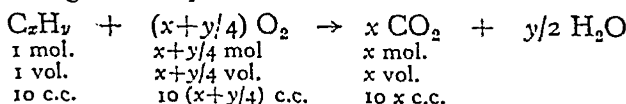
Vol. of CO_2 + unused O_2 left after explosion = 95 c.c.

Vol. of CO_2 = decrease in vol. on introducing KOH = 20 c.c.

Unused oxygen = 95−20 = 75 c.c.

Vol. of oxygen used = 100−75 = 25 c.c.

Let the formula of hydrocarbon be C_xH_y. Its oxidation will occur according to the equation



C_xH_y	+	$(x+y/4)\,O_2$	→	$x\,CO_2$	+	$y/2\,H_2O$
1 mol.		$x+y/4$ mol		x mol.		
1 vol.		$x+y/4$ vol.		x vol.		
10 c.c.		$10\,(x+y/4)$ c.c.		$10\,x$ c.c.		

As is clear from the equation above that 10 c.c. of the hydrocarbon will react with $10(x+y/4)$ c.c. of oxygen to yield $10\,x$ c.c. of CO_2. But actually 25 c.c. of oxygen is used up and 20 c.c. of carbon dioxide is produced.

∴ $10x=20$ whence $x=2$

and $10(x+y/4)=25$ or $10(2+y/4)=25$

or $2+y/4=2·5$ or $y/4=0·5$ whence $y=2$

∴ Formula of the hydrocarbon is C_2H_2 (Acetylene).

Example 7. *10 c.c. of a gaseous hydrocarbon were mixed with 100 c.c. of oxygen, and exploded in a eudiometer tube. The volume of the residual gases was 75 c.c. which was reduced to 35 c.c. on shaking with potassium hydroxide solution. What is the molecular formula of the gas ?*

Volume of the hydrocarbon $=10$ c.c.

Vol. of oxygen added $=100$ c.c.

Vol. of CO_2+unused oxygen $=75$ c.c.

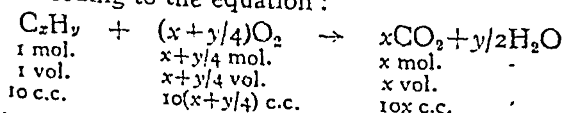
(*Gases left after explosion and cooling*)

Unused O_2=Gas left after shaking with KOH$=35$ c.c.

Vol. of $CO_2=75-35=40$ c.c.

and Vol. of oxygen used up$=100-35=65$ c.c.

Combustion of the hydrocarbon (Let its formula be C_xH_y) occurs according to the equation :



C_xH_y	+	$(x+y/4)O_2$	→	$xCO_2+y/2H_2O$
1 mol.		$x+y/4$ mol.		x mol.
1 vol.		$x+y/4$ vol.		x vol.
10 c.c.		$10(x+y/4)$ c.c.		$10x$ c.c.

As is evident from the equation, 10 c.c. of hydrocarbon require $10(x+y/4)$ c.c. oxygen for combustion, and produce $10x$ c.c. of CO_2. But actually 65 c.c. of oxygen is used up and 40 c.c. of carbon dioxide is produced.

$10x=40$ whence $x=4$

and $10(x+y/4)=65$ or $10(4+y/4)=65$.

or $4+y/4=6·5$ or $y/4=2·5$

whence $y=10$

∴ The molecular formula of the hydrocarbon is C_4H_{10} (Butane).

For more examples about the combustion of gases refer to composition of ozone, hydrochloric acid, hydrogen sulphide, sulphur dioxide, nitrous oxide, nitric oxide, ammonia and carbon dioxide in their respective chapters, Part III Non-Metals.

Case (*ii*). When the volume of oxygen added is not known but contraction in volume on combustion and cooling is known.

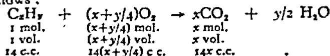
Example 8. *14 c.c. of a gaseous hydrocarbon are exploded with excess of oxygen. A volume contraction of 28 c.c. is observed. Also when the residual gases were treated with potassium hydroxide solution, a further volume contraction of 14 c.c. is observed. What is the formula of the hydrocarbon, given that the volume of the gases were measured at 0°C and 760 mm. pressure throughout.*

Volume of hydrocarbon taken = 14 c.c.

Contraction on explosion and cooling = 28 c.c.

Vol. contraction with KOH, *i.e.*, Vol. of CO_2 = 14 c.c.

Combustion of the hydrocarbon (say, C_xH_y) can be represented as follows:



$$C_xH_y + (x+y/4)O_2 \rightarrow xCO_2 + y/2\ H_2O$$

1 mol.	$(x+y/4)$ mol.	x mol.	
1 vol.	$(x+y/4)$ vol.	x vol.	
14 c.c.	$14(x+y/4)$ c.c.	$14x$ c.c.	

i.e., 14 c.c. of the hydrocarbon react with $14(x+y/4)$ c.c. of oxygen to yield $14x$ c.c. of CO_2, but actually 14 c.c. of CO_2 is produced.

$\therefore \quad 14x = 14 \quad$ whence $\quad x = 1$

Contraction in volume on combustion and cooling

$$=[14 \text{ c.c.} + 14(x+y/4) \text{ c.c.}] - 14\,x \text{ c.c.}$$

Vol. before combustion — Vol. afterwards

$$=14(1+x+y/4-x)=14(1+y/4) \text{ c.c.}$$

Equating this with the contraction in volume actually noted (=28 c.c.), we have,

$14(1+y/4)=28 \quad$ or $\quad 1+y/4=2$

whence $y/4=1 \quad$ or $\quad y=4$

$\therefore$ The molecular formula of the hydrocarbon is

CH_4 (Methane).

QUESTIONS AND PROBLEMS

Calculation of Volumes of Reacting Gases

1. 20 c.c. hydrogen, 10 c.c. carbon monoxide and 20 c.c. oxygen are exploded in a eudiometer. What would be the volume and composition of the mixture of gases left after cooling again to room temperature?

(*Senior Cambridge 1960 Dec.*)

2. The following mixtures of gases are exploded over mercury and allowed to cool, what will be the volume and composition of the resulting gas in each case? All volumes are measured at laboratory temperature and pressure.

(i) 10 c.c. of carbon monoxide and 10 c.c. of oxygen

(ii) 15 c.c. of hydrogen and 10 c.c. of oxygen.

(iii) 4 c.c. of methane (CH_4) and 20 c.c. of oxygen.

(*Senior Cambridge 1963 July*)

3. 40 c.c. of water gas, containing equal parts by volume of its constituents, is exploded with 60 c.c. of oxygen. What is the volume and composition of the resulting gaseous mixture, all volumes being measured at room temperature and pressure?

(*Senior Cambridge 1962 July*)

4. 40 ml. of hydrogen sulphide are exploded with 100 ml. of oxygen.

(i) If all volumes, before and after, are measured at N.T.P. what is the volume composition of the resulting mixture ?

(ii) If all volumes are measured at 200°C and normal pressure, what is the volume composition of the resulting mixture ? (*Senior Cambridge 1966 July*)

5. 24 ml. of water gas, containing only hydrogen and carbon monoxide in equal proportions by volume, are exploded with 80 ml. of air, 20% by volume of which is oxygen. If all the gaseous volumes are measured at room temperature and pressure, calculate the composition by volume of the resulting gaseous mixture. (*Senior Cambridge 1967 Nov.*)

Percentage Composition of a Gaseous Mixture

6. 25 c.c. of a mixture of nitrogen and nitric oxide is passed over ignited copper and the gaseous product is collected and found to occupy 20 c.c. Calculate the percentage composition of the mixture.

7. A sample of coal gas contains 50% hydrogen, 30% marsh gas, 14% carbon monoxide and 6% ethylene. One hundred cubic centimeters of the gas are mixed with 150 c.c. of oxygen, and the mixture exploded. What will be the volume and composition of the resulting gas when cooled to the original temperature ?

8. Calculate the percentage composition by volume of a mixture of carbon monoxide and methane, 10·5 c.c. of which requires 9 c.c. of oxygen for complete combustion.

9. 20 c.c. of a mixture of carbon monoxide and acetylene (C_2H_2) were fired with 30 c.c. of oxygen. The residual gas occupied 34 c.c. After treatment with caustic potash, the residual oxygen occupied 8 c.c. What was the composition of the mixture ? (*Delhi Pre-Medical 1966*)

10. A sample of gas was found to contain hydrogen, methane and carbon monoxide. 30 ml. of this mixture was exploded in a eudiometer tube with 120 ml. of oxygen. On cooling the resulting gas was found to be 102 ml. Absorption by caustic potash further reduced the volume by 15 ml. Calculate the percentage of the constituents in the mixture.
(*Punjab Pre-Medical/Pre-Engg./B.Sc. I Year 1966*)

Molecular Formula of a Gas

11. On passing electric sparks through 10 ml. ammonia taken in a eudiometer tube the volume increased to 20 ml. The resulting gas was exploded with 30 ml. oxygen and on cooling the volume was 27·5 ml. All volumes were measured under similar conditions of temperature and pressure. Vapour density of ammonia is 8·5. Calculate its molecular formula.
(*Rajasthan T.D.C. I Year 1963*)

12. 20 ml. of a gas containing only hydrogen and sulphur is heated with tin. When the reaction was over, there was no change in volume. Residual gas was hydrogen. If the molecular weight of the gas is 34, calculate its molecular formula. (*Rajasthan T.D.C. I Year 1967 Supp.*)

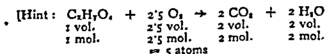
13. Find the composition of nitrous oxide from the following data :

Vol. of the gas taken	=10 c.c.
Vol. after addition of hydrogen	=28 c.c.
Vol. after explosion	=18 c.c.
Vol. after addition of oxygen	=27 c.c.
Vol. after 2nd explosion	=15 c.c.

All volumes are taken at N.T.P.

14. When 100 c.c. of a sample of ozonised oxygen were shaken with turpentine, the volume was reduced to 84 c.c. When another 100 c.c. from the same sample were heated and cooled to original temperature, the volume increased to 108 c.c. What conclusion do you draw about the composition of ozone from the above data ?

15. One volume of gaseous compound containing carbon, hydrogen and oxygen was burnt in the presence of 2·5 volumes of oxygen. On complete combustion the resultant gases contained 2 volumes of steam and 2 volumes of carbon dioxide. All volumes were measured under identical conditions. What is the formula of the compound ? (*I.I.T. Admission Test 1966*)



[Hint : $C_xH_yO_z$ + 2·5 O_2 → 2 CO_2 + 2 H_2O
1 vol. 2·5 vol. 2 vol. 2 vol.
1 mol. 2·5 mol. 2 mol. 2 mol.
= 5 atoms

16. 60 ml. of a mixture of equal volumes of chlorine and an oxide of chlorine was heated and then cooled back to the original temperature. The resulting gas mixture was found to have a volume of 75 ml. On treatment with caustic soda solution, the volume contracted to 15 ml. Assuming that all measurements were made at the same temperature and pressure, deduce the simplest formula of the oxide of chlorine. (The oxide of chlorine on heating decomposes quantitatively to oxygen and chlorine). (*I.I.T. Admission Test 1971*)

Molecular Formula of a Hydrocarbon

17. 10 c.c. of a gaseous hydrocarbon required for complete combustion 238 c.c. of air (21 per cent of oxygen by volume) and the gaseous product occupied 218 c.c. (all volumes being measured at N.T.P.). What is the empirical formula of the hydrocarbon ? (Neglect the volume of water and use approximation to the nearest whole number of the volume of oxygen.) (*Punjab Inter. 1961*)

18. 15 c.c. of a gaseous hydrocarbon were exploded with 105 c.c. of oxygen. After cooling the residual gas occupied 75 c.c. On treatment with strong solution of caustic potash the volume was further reduced to 30 c.c. Determine the molecular formula of the hydrocarbon, name it and write structural formula. (*Punjab Pre-Engg /Pre-Medical/I Year Degree 1962*)

19. 20 c.c. of a hydrocarbon C_xH_y were exploded with 200 c.c of [illegible] ment with [illegible] of x and y. [illegible] *Year 1965*)

20. 20 ml. of a gaseous hydrocarbon was exploded with excess of oxygen in a eudiometer tube. On cooling the volume of resultant gases was reduced by 50 ml. On further treatment with KOH solution there was a further contraction of 40 ml. Calculate the molecular formula of the hydrocarbon (*Punjab Pre-Engg./Pre-Medical/B.Sc I Year 1967*)

21. 10 ml. of a gaseous hydrocarbon are mixed with 30 ml. of oxygen in a eudiometer tube and exploded. After cooling the residual gas occupied 20 ml. On addition of KOH there was further contraction to 10 ml Find the formula of the hydrocarbon. (*Punjab Inter. 1960*)

22. 12 c.c. of gaseous hydrocarbon were exploded with excess of oxygen. On explosion and cooling there was contraction of 30 c.c. On addition of KOH there was a further contraction in volume by 24 c.c. Calculate the molecular formula of the gaseous hydrocarbon. All volumes are measured at the same temperature and pressure. (*Ajmer Inter. 1962*)

23. 30 c.c. of oxygen were required for the complete combustion of 10 c.c. of a gaseous hydrocarbon. After the combustion, the gaseous mixture was found to occupy 20 c.c. and the whole gas was completely absorbed by caustic potash. What is the empirical formula of the hydrocarbon ? (*Nagpur Pre-University 1971*)

4. 40 ml. of hydrogen sulphide are exploded with 100 ml. of oxygen.

(i) If all volumes, before and after, are measured at N.T.P. what is the volume composition of the resulting mixture ?

(ii) If all volumes are measured at 200°C and normal pressure, what is the volume composition of the resulting mixture ? *(Senior Cambridge 1966 July)*

5. 24 ml. of water gas, containing only hydrogen and carbon monoxide in equal proportions by volume, are exploded with 80 ml. of air, 20% by volume of which is oxygen. If all the gaseous volumes are measured at room temperature and pressure, calculate the composition by volume of the resulting gaseous mixture. *(Senior Cambridge 1967 Nov.)*

Percentage Composition of a Gaseous Mixture

6. 25 c.c. of a mixture of nitrogen and nitric oxide is passed over ignited copper and the gaseous product is collected and found to occupy 20 c Calculate the percentage composition of the mixture.

7. A sample of coal gas contains 50% hydrogen, 30% marsh gas, 14 carbon monoxide and 6% ethylene. One hundred cubic centimeters of the g are mixed with 150 c.c. of oxygen, and the mixture exploded. What will be t volume and composition of the resulting gas when cooled to the origi temperature ?

8. Calculate the percentage composition by volume of a mixture carbon monoxide and methane, 10·5 c.c. of which requires 9 c.c. of oxygen f complete combustion.

9. 20 c.c. of a mixture of carbon monoxide and acetylene (C_2H_2) we fired with 30 c.c. of oxygen. The residual gas occupied 34 c.c. After treatme with caustic potash, the residual oxygen occupied 8 c.c. What was the compo tion of the mixture ? *(Delhi Pre-Medical 19*

10. A sample of gas was found to contain hydrogen, methane and c bon monoxide. 30 ml. of this mixture was exploded in a eudiometer tube w 120 ml. of oxygen. On cooling the resulting gas was found to be 102 r Absorption by caustic potash further reduced the volume by 15 ml. Calcul the percentage of the constituents in the mixture.

(Punjab Pre-Medical/Pre-Engg./B.Sc. I Year 19

Molecular Formula of a Gas

11. On passing electric sparks through 10 ml. ammonia taken in eudiometer tube the volume increased to 20 ml. The resulting gas was explod with 30 ml. oxygen and on cooling the volume was 27·5 ml. All volumes we measured under similar conditions of temperature and pressure. Vapour de sity of ammonia is 8·5. Calculate its molecular formula.

(Rajasthan T.D.C. I Year 19

12. 20 ml. of a gas containing only hydrogen and sulphur is heated w tin. When the reaction was over, there was no change in volume. Resid gas was hydrogen. If the molecular weight of the gas is 34, calculate molecular formula. *(Rajasthan T.D.C. I Year 1967 Sup*

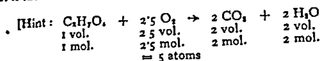
13. Find the composition of nitrous oxide from the following data :

Vol. of the gas taken	=10 c.c.
Vol. after addition of hydrogen	=28 c.c.
Vol. after explosion	=18 c.c.
Vol. after addition of oxygen	=27 c.c.
Vol. after 2nd explosion	=15 c.c.

All volumes are taken at N.T.P.

14. When 100 c.c. of a sample of ozonised oxygen were shaken w turpentine, the volume was reduced to 84 c.c. When another 100 c.c. from t same sample were heated and cooled to original temperature, the volu increased to 108 c.c. What conclusion do you draw about the composition ozone from the above data ?

15. One volume of gaseous compound containing carbon, hydrogen and oxygen was burnt in the presence of 2·5 volumes of oxygen. On complete combustion the resultant gases contained 2 volumes of steam and 2 volumes of carbon dioxide. All volumes were measured under identical conditions. What is the formula of the compound ? *(I.I.T. Admission Test 1966)*



[Hint : $C_xH_yO_z$ + 2·5 O_2 → 2 CO_2 + 2 H_2O
1 vol. 2·5 vol. 2 vol. 2 vol.
1 mol. 2·5 mol. 2 mol. 2 mol.
= 5 atoms

16. 60 ml of a mixture of equal volumes of chlorine and an oxide of chlorine was heated and then cooled back to the original temperature. The resulting gas mixture was found to have a volume of 75 ml. On treatment with caustic soda solution, the volume contracted to 15 ml. Assuming that all measurements were made at the same temperature and pressure, deduce the simplest formula of the oxide of chlorine. (The oxide of chlorine on heating decomposes quantitatively to oxygen and chlorine). *(I.I.T. Admission Test 1971)*

Molecular Formula of a Hydrocarbon

17. 10 c.c. of a gaseous hydrocarbon required for complete combustion 238 c.c. of air (21 per cent of oxygen by volume) and the gaseous product occupied 218 c.c. (all volumes being measured at N.T.P.). What is the empirical formula of the hydrocarbon ? (Neglect the volume of water and use approximation to the nearest whole number of the volume of oxygen.) *(Punjab Inter. 1961)*

18. 15 c.c. of a gaseous hydrocarbon were exploded with 105 c.c. of oxygen. After cooling the residual gas occupied 75 c.c. On treatment with strong solution of caustic potash the volume was further reduced to 30 c.c. Determine the molecular formula of the hydrocarbon, name it and write structural formula. *(Punjab Pre-Engg /Pre-Medical/I Year Degree 1962)*

19. 20 c.c. of a hydrocarbon C_xH_y were exploded with 200 c.c. of oxygen. ... On treatment with ... of x and y ... *Year 1965)*

20. 20 ml. of a gaseous hydrocarbon was exploded with excess of oxygen in a eudiometer tube. On cooling the volume of resultant gases was reduced by 50 ml. On further treatment with KOH solution there was a further contraction of 40 ml. Calculate the molecular formula of the hydrocarbon. *(Punjab Pre-Engg /Pre-Medical/B.Sc I Year 1967)*

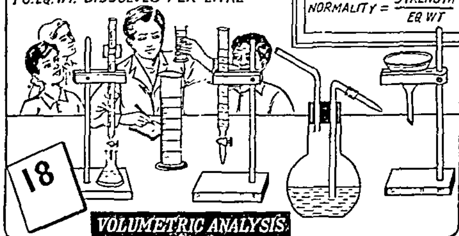
21. ... mixed with ... ml of oxygen ...

22. 12 c.c. of gaseous hydrocarbon were exploded with excess of oxygen. On explosion and cooling there was contraction of 30 c.c. On addition of KOH there was a further contraction in volume by 24 c.c. Calculate the molecular formula of the gaseous hydrocarbon. All volumes are measured at the same temperature and pressure. *(Ajmer Inter. 1962)*

23. 30 c.c. of oxygen were required for the complete combustion of 10 c.c. of a gaseous hydrocarbon. After the combustion, the gaseous mixture was found to occupy 20 c.c. and the whole gas was completely absorbed by caustic potash. What is the empirical formula of the hydrocarbon ? *(Nagpur Pre-University 1971)*

ANSWERS

1. Oxygen=5 c.c. ; carbon dioxide=10 c.c. ; Total=15 c.c.
2. (i) CO_2=10 c.c. ; O_2=5 c.c. ; Total=15 c.c.
   (ii) 2·5 c.c. oxygen.
   (iii) CO_2=4 c.c. ; O_2=12 c.c. ; Total=16 c.c.
3. CO_2=20 c.c. ; O_2=40 c.c. ; Total=60 c.c.
4. (i) SO_2=40 ml. ; O_2=40 ml.
   (ii) SO_2=40 ml. ; O_2=40 ml. ; Steam=40 ml.
5. N_2=64 ml. ; O_2=4 ml. ; CO_2=12 ml.
6. N_2=60% ; NO=40%.
7. Unused oxygen=40 c.c. ; CO_2=56 c.c. ; Total=96 c.c.
8. CO=76·19% ; CH_4=23·81%.
9. CO=14 c.c. ; C_2H_2=6 c.c.
10. H_2=50% ; CH_4=40% ; CO=10%.
11. NH_3. 12. H_2S. 13. N_2O. 14. O_3.
15. C_2H_4O. 16. Cl_2O. 17. C_3H_8.
18. C_3H_8 ; propane ; $CH_3-CH_2-CH_3$.
19. C_2H_2 (*Ethyne*). 20. C_2H_6.
21. CH_4. 22. C_2H_6. 23. C_2H_4.



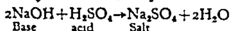
Volumetric Analysis

1. Problems based on Volumetric Analysis.—All volumetric experiments are based on one chemical reaction or the other. The reactants are taken in the form of solutions and made to react. A known volume of one solution is measured with a pipette and taken in a conical flask. The other solution is taken in a burette (Fig. 18·1) and run into the first solution till the chemical reaction is just complete. The volume of the second solution is read from the burette and the two volumes are compared.

2. Terms Used.—Various terms used in volumetric analysis are given below :

(i) Titration. The process of adding one solution from the burette to another in the conical flask, in order to complete the chemical reaction involved, is termed *titration*.

(ii) Acidimetry and Alkalimetry. The branch of volumetric analysis involving chemical reaction between an acid and a base is called *Acidimetry and Alkalimetry*.



$$\underset{\text{Base}}{2NaOH}+\underset{\text{acid}}{H_2SO_4}\rightarrow\underset{\text{Salt}}{Na_2SO_4}+2H_2O$$

(iii) Oxidation Titrations. These are based upon the chemical reaction between acidified potassium permanganate or potassium dichromate and a reducing agent, *e.g.*, oxalic acid or ferrous sulphate.

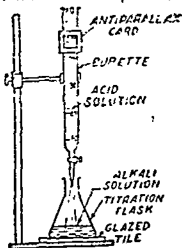


Fig. 18·1.

(iv) Silver Nitrate Titrations. These include the chemical reactions between a soluble chloride and silver nitrate.

(*v*) **End Point.** It is the exact stage at which the chemical reaction involved in the titration is just complete.

(*vi*) **Indicator.** It is a substance used to indicate the end point. For example, phenolphthalein and methyl orange are indicators used in acid-alkali titrations. Potassium chromate is used as an indicator in silver nitrate titrations while potassium permanganate itself acts as an indicator in potassium permanganate titrations.

(*vii*) **Standard Solution.** A solution of known strength is termed a *standard solution*. For example, a 3% solution of copper sulphate is a standard solution.

(*viii*) **Normal Solution.** A solution containing 1 gm. eq. wt. of the solute dissolved per litre is called a *normal solution*. Thus, a normal solution of sodium hydroxide contains 40 gm. of it dissolved per litre and is written as N-NaOH.

(*ix*) **Sub-normal solution.** A solution containing a fraction of gram eq. wt. of the solute dissolved per litre is called a sub-normal solution. For example, a semi-normal solution of sodium hydroxide contains 20 gm. ($\frac{1}{2}$ fraction of gm. eq. wt.) of sodium hydroxide dissolved per litre. It is written as N/2 or 0·5 N-NaOH. Similarly a decinormal sodium hydroxide solution contains 4 gm. ($\frac{1}{10}$ fraction of gm. eq. wt.) of sodium hydroxide dissolved per litre. It is written as N/10 or 0·1 N-NaOH.

(*x*) **Normality.** The ratio between gm./litre and eq. wt. of a solute is called *normality factor*. For example, normality of a solution of sodium hydroxide containing 5 gm./litre

$$=5/40=1/8 \text{ or } 0{\cdot}125.$$

(*xi*) **Molar Solution.** A solution containing 1 gm. mol. wt. of the solute dissolved per litre is called its molar solution. For example, the molar solution of sulphuric acid contains 98 gm./litre, while its normal solution contains 49 gm. of it per litre.

(*xii*) **Normality Equation.** It is an expression of the result of a titration in the form of an equation. For example, writing the normality equation for the titration wherein 10 ml. of an alkali of an unknown normality (say, N′) neutralize 12·5 ml. of N/8 HCl, we have

$$10 \text{ ml. of } N'\text{-NaOH} \equiv 12{\cdot}5 \text{ ml. of N/8 HCl}.$$

(*xiii*) **Normality Formula.** In the titration

$$V_1 \text{ ml. of } N_1\text{-NaOH} \equiv V_2 \text{ ml. of } N_2\text{-HCl}$$

$N_1 \times V_1$ gives the milli-equivalents of the sodium hydroxide present in V_1 ml. of N_1-NaOH. Similarly, $N_2 \times V_2$ give the milli-equivalents of the hydrochloric acid present in V_2 ml. of N_2-HCl. According to the law of equivalent weights, *substances react in the ratio of their equivalent weights.*

Or x milli-equivalents of sodium hydroxide will react with x (same number) milli-equivalents of hydrochloric acid.

$$N_1V_1 = N_2V_2 \text{ (Normality Formula)}$$

3. Calculation of Equivalent weights from Formula.

(i) Eq. wt. of an acid $= \frac{\text{Molecular weight}}{\text{Basicity}}$

where basicity is the number of replaceable hydrogen atoms present in one molecule of the acid, *e.g.*, basicity of HCl, H_2SO_4 and H_3PO_4 is 1, 2 and 3 respectively.

(ii) Eq. wt. of a base $= \frac{\text{Molecular weight}}{\text{Acidity}}$

where acidity is the number of replaceable OH groups present in one molecule of the base, *e.g.*, acidity of NaOH, $Ba(OH)_2$ and $Fe(OH)_3$ is 1, 2 and 3 respectively.

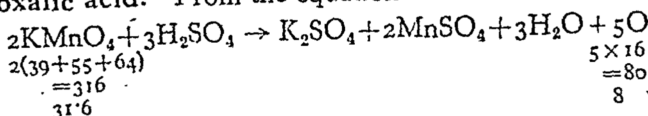
(iii) Eq. wt. of a salt taking part in an acid-alkali titration is calculated by making use of the law of equivalents or using the general formula :

$$\text{Eq. wt. of an acid, base or a salt} = \frac{\text{Molecular weight}}{\text{Total positive valencies}}$$

Example 1. *Calculate the equivalent weight of (a) hydrochloric acid, (b) sulphuric acid, (c) anhydrous oxalic acid, (d) crystalline oxalic acid, (e) caustic soda, (f) caustic potash, (g) sodium carbonate, (h) sodium bicarbonate, and (i) calcium carbonate.*

Substance	Formula	Mol. wt.	Total positive valencies (=x)	Eq. wt. = $\frac{\text{Mol. wt.}}{x}$
(a) Hydrochloric acid	HCl	36·5	1(H^+)	$\frac{36.5}{1} = 36.5$
(b) Sulphuric acid	H_2SO_4	98	2(H^+)	$\frac{98}{2} = 49$
(c) Oxalic acid (anhydrous)	$(COOH)_2$	90	2($2H^+$)	$\frac{90}{2} = 45$
(d) Oxalic acid (crystals)	$(COOH)_2 \cdot 2H_2O$	126	2($2H^+$)	$\frac{126}{2} = 63$
(e) Caustic soda	NaOH	40	1(Na^+)	$\frac{40}{1} = 40$
(f) Caustic potash	KOH	56	1(K^+)	$\frac{56}{1} = 56$
(g) Sodium carbonate	Na_2CO_3	106	2($2Na^+$)	$\frac{106}{2} = 53$
(h) Sodium bicarbonate	$NaHCO_3$	84	1(Na^+)	$\frac{84}{1} = 84$
(i) Calcium carbonate	$CaCO_3$	100	2(Ca^{++})	$\frac{100}{2} = 50$

(*iv*) Eq. wt. of potassium permanganate, ferrous salts and oxalic acid. From the equation

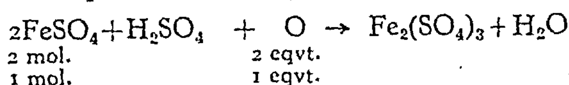


$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5O$$

$2(39+55+64) = 316$; $31·6$ — $5\times16 = 80$; 8

It is clear that 316 parts by weight of $KMnO_4$ liberate 80 parts by weight (10 equivalents) of oxygen. *Or* 31·6 parts by weight of $KMnO_4$ liberate 8 parts by weight (1 equivalent) of oxygen.

∴ Eq. wt. of $KMnO_4$=31·6.



$$2FeSO_4+H_2SO_4 + O \rightarrow Fe_2(SO_4)_3+H_2O$$

2 mol. — 2 eqvt.
1 mol. — 1 eqvt.

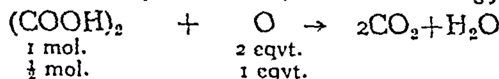
It this equation, 2 mol. of $FeSO_4$ react with 1 atom (2 equivalents) of oxygen. *Or* 1 mol. of $FeSO_4$ reacts with 1 equivalent of oxygen.

∴ Eq. wt. of ferrous sulphate =Its Molecular wt.

Eq. wt. of $FeSO_4$ (*anhydrous*) $=56+32+64=152$

Eq. wt. of $FeSO_4.7H_2O$ (*crystals*) $=152+7\times18=278$

Eq. wt. of $FeSO_4.(NH_4)_2SO_4.6H_2O$ (*Mohr's salt*) $=152+132+6\times18 =392$



$$(COOH)_2 + O \rightarrow 2CO_2+H_2O$$

1 mol. — 2 eqvt.
½ mol. — 1 eqvt.

In the above equation 1 equivalent of oxygen oxidises ½ mol of oxalic acid. Hence equivalent weight of oxalic acid is half its mol. wt.

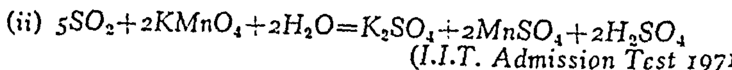
Eq. wt. of $(COOH)_2$ (*anhydrous*) $=90/2=45$

Eq. wt. of $(COOH)_2.2H_2O$ (*crystals*) $=126/2=63$

Example 2. *Calculate the equivalent weight of sulphur dioxide in the following reactions :*



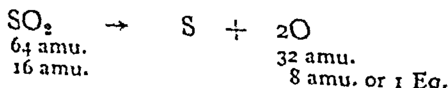
(i) $SO_2+2H_2S=3S+2H_2O$



(ii) $5SO_2+2KMnO_4+2H_2O=K_2SO_4+2MnSO_4+2H_2SO_4$

(*I.I.T. Admission Test 1971*)

In (*i*) SO_2 is being reacted by H_2S to S and the change can be represented as



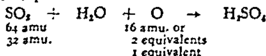
$$SO_2 \rightarrow S + 2O$$

64 amu. — 32 amu.
16 amu. — 8 amu. or 1 Eq.

From the equation we find that 16 amu. of SO_2 gives 8 amu. equivalent of nascent oxygen.

Eq. wt. of SO_2=16.

In (*ii*) SO_2 is being oxidised by $KMnO_4$ to H_2SO_4 and the change can be represented as



$$SO_2 + H_2O + O \rightarrow H_2SO_4$$

64 amu   16 amu. or
32 amu.   2 equivalents
    1 equivalent

From the equation we learn that 64 amu. of SO_2 react with 16 amu. or 2 equivalents of nascent oxygen.

Or 32 amu. of SO_2 reacts with 8 amu. or 1 equivalent of nascent oxygen.

$\therefore$ Eq. wt. of SO_2=32.

4. Calculation of Normality.

Example 3. *Calculate the normality of the following solutions.*

(*i*) *H_2SO_4 solution containing 7 gm./litre.*

(*ii*) *KOH solution containing 2·8 gm./litre.*

(*iii*) *Oxalic acid solution containing 1·26 gm./litre.*

(*iv*) *$KMnO_4$ solution containing 6·32 gm./litre.*

(*i*) Eq. wt. of H_2SO_4=Mol. wt /2=49.

Strength=7 gm /litre.

$$\text{Normality}=\frac{\text{Strength}}{\text{Eq. wt.}}=\frac{7}{49}=\frac{1}{7} \text{ or } 0{\cdot}143.$$

(*ii*) Eq. wt. of KOH =Mol. wt./1 =56

Strength=2·8 gm./litre

$$\text{Normality}=\frac{\text{Strength}}{\text{Eq. wt.}}=\frac{2{\cdot}8}{56}=\frac{1}{20} \text{ or } 0{\cdot}05.$$

(*iii*) Eq. wt. of oxalic acid crystals, $(COOH)_2.2H_2O$

=Mol. wt./2=126/2=63

Strength=1·26 gm./litre

$$\text{Normality}=\frac{\text{Strength}}{\text{Eq. wt.}}=\frac{1{\cdot}26}{63}=\frac{1}{50} \text{ or } 0{\cdot}02.$$

(*iv*) Eq. wt. of $KMnO_4$=31·6 (*see* page 1·170)

Strength=6·32 gm./litre

$$\text{Normality}=\frac{6{\cdot}32}{31{\cdot}6}=\frac{1}{5} \text{ or } 0{\cdot}2.$$

Example 4. *25·0 c.c. of an acid solution were found by titration to neutralize 22·2 c.c. of 0·12 N sodium hydroxide solution. Find the normality of the acid.*

Let the normality of the acid be N′. Writing the normality equation, we have

25·0 c.c. of N′-acid soln.≡22·2 of 0·12 N-NaOH soln.

Applying normality formula, $N_1V_1=N_2V_2$, we have

$$25N'=22{\cdot}2\times0{\cdot}12$$

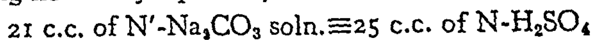
or $$N'=\frac{22{\cdot}2\times0{\cdot}12}{25}=0{\cdot}1066$$

5. Calculation of Strength.

Example 5. *If 25 c.c. of normal sulphuric acid neutralized 21 c.c. of a solution of sodium carbonate, calculate the strength of sodium carbonate solution.*

Let N′ be the normality of sodium carbonate solution.

Writing normality equation, we have


21 c.c. of N′-Na_2CO_3 soln.≡25 c.c. of N-H_2SO_4

Applying normality formula, $N_1V_1=N_2V_2$, we have

$$21N'=25\times1$$

or $$N'=25/21=1{\cdot}19.$$

$$\text{Eq. wt. of } Na_2CO_3=\frac{\text{Mol. wt.}}{\text{Total positive valency}}=\frac{106}{2}=53.$$

Strength of sodium carbonate in grams per litre

=normality factor × equivalent weight

=1·19 × 53=63·07 gm./litre

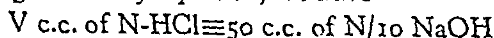
Strength in terms of normality=1·19 N.

6. Calculation of Equivalent Weight.

Example 6. *One gm. of the carbonate of a metal was dissolved in 25 c.c. normal HCl. The resulting liquid required 25 c.c. N/10 caustic soda solution to neutralize it completely. Calculate the equivalent weight of the carbonate and the metal.*

A part of the 25 c.c. N-HCl is neutralized by the carbonate and the part left unreacted (say, V c.c.) requires 50 c.c. N/10 NaOH for complete neutralization.

Writing normality equation, we have


V c.c. of N-HCl≡50 c.c. of N/10 NaOH

Applying normality formula, $N_1V_1=N_2V_2$, we have

$$V\times1=50\times\frac{1}{10}=5$$

∴ V, the volume of acid left=5 c.c. N-HCl and

Volume of acid used by the carbonate=(25−5)=20 c.c. N-HCl.

Now, 20 c.c. N-HCl≡1 gm. of the carbonate.

∴ 1000 ,, ,, $\equiv\frac{1}{20}\times1000=50$ gm. of the carbonate

∴ Eq. wt. of the metal carbonate=50.

Now Eq. wt. of metal=$E_{MCO_3}-E_{CO_3}$

=50−30=20.

[Eq. wt. of CO_3 radical=Its weight/valency=60/2=30]

7. Molecular Weights of Acids and Bases.

Mol. wt. of an acid = Eq. wt. × Basicity

Mol. wt. of a base = Eq. wt. × Acidity.

Example 7. *20 c.c. of a solution containing 6·5 gm. of a dibasic acid per litre neutralized 22·18 c.c. of a solution of sodium hydroxide. The same volume (20 c.c.) of N/10-HCl neutralized 21·5 c.c. of the same NaOH solution. Calculate the molecular weight of the acid.* (Delhi H.S. 1966)

Let N′ be the normality of the dibasic acid solution containing 6·5 gm. per litre and N″ be the normality of NaOH solution.

Writing the normality equation for HCl and NaOH titration, we have

21·5 c.c. of N″-NaOH ≡ 20 c.c. of N/10 HCl.

Applying normality formula, $N_1V_1 = N_2V_2$, we get

$$21 \cdot 5N'' = 20 \times 1/10$$

whence $$N'' = \frac{20}{10 \times 21 \cdot 5} = \frac{1}{10 \cdot 75}$$

Writing the normality equation for dibasic acid and NaOH titration :

20 c.c. of N′-acid solution ≡ 22·18 c.c. of N/10·75 NaOH.

Applying the normality formula again

$$20\ N' = 22 \cdot 18 \times \frac{1}{10 \cdot 75}$$

or $$N' = \frac{22 \cdot 18}{20 \times 10 \cdot 75} = 0 \cdot 1031$$

Equivalent weight $= \frac{\text{Grams per litre}}{\text{Normality factor}} = \frac{6 \cdot 5}{0 \cdot 1031} = 63 \cdot 04$

Molecular weight = *Eq. wt.* × *Basicity*

= 63·04 × 2 = 126·08.

8. Percentage Composition of a mixture.

Example 8. *A sample of sodium carbonate was found to contain some sodium sulphate. 1·25 gm. of this sample were dissolved in water and made up to 250 c.c.; 25 c.c. of this solution required 20 c.c. of N/10 sulphuric acid solution for exact neutralization. Calculate the percentage of sodium sulphate in the given sample of sodium carbonate.*

Wt. of sample present in 250 c.c. = 1·25 gm.

" " " per litre $= 1 \cdot 25 \times \frac{1000}{250} = 5$ gm.

Let its normality be N′. Writing normality equation for the titration in which only Na_2CO_3 reacts :

25 c.c. of N′-Na_2CO_3 ≡ 20 c.c. of N/10 H_2SO_4

Applying normality formula, $N_1V_1=N_2V_2$, we have

$$25\times N'=20\times 1/10$$

or
$$N'=\frac{20}{10\times 25}=\cdot 08$$

Strength of $Na_2CO_3=\cdot 08\times 53=4\cdot 24$ gm./litre.

∴ 5 gm. of the sample dissolved per litre contains 4·24 gm. of Na_2CO_3 and $5-4\cdot 24=0\cdot 76$ gm. per litre of Na_2SO_4.

Percentage of Na_2SO_4 in the sample $=\frac{0\cdot 76}{5}\times 100=15\cdot 2$.

9. Percentage Purity of a Sample.

Example 9. *1·20 gm. of a commercial sample of oxalic acid, $C_2H_2O_4.2H_2O$, were dissolved in 200 c.c. of water. 10 c.c. of this solution required 8·5 c.c. of decinormal potassium permanganate solution for complete oxidation. Calculate the percentage purity of the sample.*

1·2 gm. of the oxalic acid sample are dissolved in 200 c.c. The weight of sample, therefore, present per litre $=1\cdot 2\times 5=6$ gm.

Let the normality of this solution be N′.

Writing normality equation, we have

10 c.c. of N′-oxalic acid ≡ 8·5 c.c. of N/10 $KMnO_4$ solution.

Applying normality formula, $N_1V_1=N_2V_2$, we get

$$10N'=8\cdot 5\times 1/10$$

or
$$N'=\frac{8\cdot 5}{10\times 10}=\cdot 085$$

$$\text{Equivalent weight of } C_2H_2O_4.2H_2O=\frac{\text{Mol. wt.}}{\text{Basicity}}=\frac{126}{2}=63$$

$$\text{Strength}=\text{Eq. wt.}\times\text{Normality factor}$$
$$=63\times\cdot 085 \text{ gm./litre}$$

$$\text{Percentage purity of the sample}=\frac{63\times\cdot 085}{6}\times 100=89\cdot 25.$$

10. Preparation of Standard Solution by Dilution.

Example 10. *20 c.c. of a solution of sulphuric acid neutralizes 21·2 c.c. of 3% solution of sodium carbonate. How much water should be added to each 100 c.c. of the solution to reduce its strength to decinormal?*

Given 3% solution of sodium carbonate contains 30 gm. of it per litre.

$$\text{Normality of the solution}=\frac{\text{Grams per litre}}{\text{Equivalent weight}}=\frac{30}{53}=0\cdot 566$$

Let the normality of acid solution be N′. Writing normality equation for the titration, we have

20 c.c. of N'-acid solution≡21·2 c.c. of 0·566 N-Na_2CO_3.

Applying the normality formula, $N_1V_1=N_2V_2$, we get

$$20 \times N' = 21 \cdot 2 \times 0 \cdot 566$$

whence $$N' = \frac{21 \cdot 2}{20} \times 0 \cdot 566 = 0 \cdot 6$$

Let 100 c.c. of the solution be diluted to V c.c. in order to reduce its strength to decinormal. Here

100 c.c. of 0·6 N-H_2SO_4≡V c.c. of N/10 H_2SO_4.

Applying normality formula again,

$$100 \times 0 \cdot 6 = V \times 1/10$$

or $$V = 100 \times 0 \cdot 6 \times 10 = 600 \text{ c.c.}$$

i.e., if 100 c.c. of the 0·6 N solution be diluted to 600 c.c., its strength will be reduced to N/10.

∴ Vol. of water to be added to each 100 c.c. of the solution =(600−100)=500 c.c.

11. Miscellaneous Calculations

Example 11. *1·575 gm. of $(COOH)_2.xH_2O$ are dissolved in water and the volume made up to 250 ml On titration 16·68 ml. of the solution are required for exact neutralization of 25 ml. of N/15 NaOH solution. Calculate the value of x.*

Strength of oxalic acid $= 1 \cdot 575 \times \frac{1000}{250} = 6 \cdot 3$ gm./litre

Let its normality be N'.

Writing normality equation .

16·68 ml. of N'-oxalic acid≡25 ml. of N/15 NaOH

Applying normality formula, $N_1V_1=N_2V_2$, we get

$$16 \cdot 68 \times N' = 25 \times 1/15$$

whence $$N' = \frac{25}{15 \times 16 \cdot 68} = 0 \cdot 1$$

Eq. wt. of hydrated acid $= \frac{\text{Gm./litre}}{\text{Normality}} = \frac{6 \cdot 3}{0 \cdot 1} = 63$

Eq. wt. of $(COOH)_2.xH_2O$ from the formula

$$= \frac{\text{Mol. wt.}}{2} = \frac{90+18x}{2} = 45+9x$$

Equating this with the eq. wt. as calculated from titration data, we have

$$45+9x=63$$

whence $$x = \frac{63-45}{2} = 2.$$

QUESTIONS AND PROBLEMS

1. Explain the following terms :

Titration	Standard solution	Normality equation
End point	Normal solution	Normality formula
Indicator	Molar solution	Basicity of an acid
Normality	Sub-normal solution	Law of equivalents

Standard Solutions

2. Calculate the amount of each substance present in the following solutions :—

(i) 250 c.c. of 0·12 N-H_2SO_4 solution. *(Bombay I Year Science 1963)*

(ii) 100 c.c. of 0·15 N-$NaHCO_3$ solution. *(Bombay I Year Science 1963)*

(iii) 1 litre of N/10 anhydrous and hydrated [crystalline, $(COOH)_2.2H_2O$] oxalic acid solutions.

(iv) 1 litre of the normal solution of (a) Potassium permanganate, (b) Potassium dichromate. *(Punjab Inter. 1966 Supp.)*

(v) 200 ml. of 0·1 N solution of potassium permanganate. *(Delhi Pre-Medical 1960)*

(vi) 500 c.c. of 1·5 N-H_2SO_4 and 1·5 N-Na_2CO_3 solution. *(I.I.T. Admission Test 1961)*

(vii) 100 c.c. of 10 N-NaCl. *(Delhi H.S. 1963)*

3. Calculate the Normality of the following solutions containing—

(i) 12·6 gm. of nitric acid in 200 c.c. of solution.

(ii) 21·2 gm. of anhydrous sodium carbonate in 500 c.c. of solution ? *(Senior Cambridge 1964 Dec.)*

4. Specific gravity of a given sample of sulphuric acid is 1·51 and it contains 60·65% by weight of pure sulphuric acid. What volume of this sample is required to prepare one litre of normal sulphuric acid ? *(Bihar H.S. 1966)*

5. Concentrated sulphuric acid has a density of 1·84 g./ml. at 25°C and contains 98% of acid by weight. What volume of the concentrated acid should be used to prepare 1000 litres of 0·5 molar sulphuric acid solution at 25°C ? *(I.I.T. Admission Test 1971)*

[Hint : Molar solution of sulphuric acid contains 98 g. of acid dissolved per litre of solution].

Strength of a Solution

6. 25 c.c. of 0·82 N-NaOH was added to 50 c.c. HCl solution. Excess of the acid required 30 c.c. of 0·09 N-Na_2CO_3 solution for titration. Calculate the strength of the acid in terms of normality as well as grams per litre. *(Bihar H.S. 1964)*

[Hint : 25 c.c. of 0·82 N-NaOH$\equiv 25\times 0{\cdot}82 = 20{\cdot}5$ c.c. of N-alkali.
30 c.c. of 0·09 N-$Na_2CO_3 \equiv 30\times 0{\cdot}09 = 2{\cdot}7$ c.c. of N-alkali.
50 c.c. N-HCl$\equiv 20{\cdot}5 + 2{\cdot}7 = 23{\cdot}2$ c.c. of N-alkali.]

7. What will be the volume of a 3 per cent sodium carbonate solution for neutralization of a litre of N/10 sulphuric acid ? *(I.I.T. Admission Test 1960)*

8. 18 c.c. N/2 HCl and 20·6 c.c. 2N-HCl are added to 16·4 c.c. N/10 HCl. Calculate the strength of the mixture in terms of normality as well as grams per litre. *(Bihar H.S. 1964 Supp.)*

9. 0·5 gm of pure calcium carbonate was found to require 15 c.c. of dilute hydrochloric acid for complete neutralization. Calculate the normality of the acid. *(Punjab Inter. 1960)*

10. 25 c.c. of a solution of hydrochloric acid containing 7·3 gm. of the acid per litre neutralized 30 c.c. of caustic soda solution. 20 c.c. of this alkali solution neutralized 24 c.c. of a solution of sulphuric acid. Calculate the normality and strength of sulphuric acid. *(Delhi H.S. 1963)*

Eq. Wt. from Titration Data

11. 25 c.c. of a deci-normal solution of hydrochloric acid exactly neutralized 20 c.c. of a solution of a base containing 4·8 gm. per litre of the base. Find out the equivalent weight of the base. *(Delhi H.S. 1960)*

12. 0·225 g. of oxalic acid requires 50 c.c. of 0·1 N-$KMnO_4$, solution for complete oxidation. What is the equivalent weight of oxalic acid? *(I.I.T. Admission Test 1966)*

13. A sample of organic acid weighing 3·00 grams was dissolved in water. Using a suitable indicator, it was titrated with 0·5N sodium hydroxide solution. Exactly 40·0 c.c. were required for neutralization. What is the equivalent weight of the acid? *(I.I.T. Admission Test 1964)*

Percentage Composition

14. 3·0 gm. of a mixture of NaCl and NaOH were dissolved in distilled water to make 250 c.c. of the solution. 20 c.c. of this solution required 24 c.c. of HCl for neutralization and 18 c.c. of this HCl required 20 c.c. of N/10 KOH solution. Find the percentage composition of the mixture.

15. 0·6 gm. of limestone were dissolved in 50 c.c. of N/10 HCl and the solution made up to 100 c.c. 25 c.c. of this solution required 12·5 c.c. of N/25 NaOH. Calculate the percentage of calcium carbonate in the limestone sample. *(U.P. Board Inter. 1964)*

Percentage Purity

16. A 0·56 g. sample of limestone is dissolved in acid and the calcium precipitated as calcium oxalate, CaC_2O_4. After filtering and washing the precipitate, it requires 40 c.c. of 0·25 N-$KMnO_4$ solution for titration in acidic medium. Calculate the per cent CaO in the limestone. *(I.I.T. Admission Test 1966)*

[Hint: 1000 c.c. N-$KMnO_4$≡64 gm. CaC_2O_4≡28 gm. CaO.]

17. 0·5 gram of an oxalate was dissolved in water and the solution made to 100 ml. On titration 10 ml. of this solution required 15 ml. of N/20 $KMnO_4$. Calculate the percentage of oxalate in the sample. *(U.P. Board Inter. 1967)*

Molecular Weights of Acids and Bases

18. Calculate the molecular weight of a dibasic acid, 0·45 gm. of which required 200 c.c. of N/20 sodium hydroxide solution for neutralization. (At. wt. of sodium = 23) *(Delhi H.S. 1967)*

19. 0·84 gm. of an acid of mol. wt. = 150 is dissolved in 100 c.c. water and 25 c.c. of the solution required 28 c.c. of N/10 NaOH solution for titration. Calculate the basicity of the acid. *(Bihar H.S. 1965 Supp.)*

20. 20 ml. of a decinormal solution of NaOH neutralises 25 ml. of the solution of a dibasic acid containing 6·0 gm. of the acid per litre. Find the equivalent weight and the molecular weight of the acid. *(Delhi H.S. 1970)*

Number of Molecules, Water of Crystallization

21. 1·578 gm. of crystalline barium hydroxide was dissolved in water and the solution required 40 c.c. N/4 HNO_3 for complete neutralization. Calculate the number of molecules of water present in gram molecule of the base (Ba = 137·4).

Double Titration

22. 25 c.c. of a solution of hydrochloric acid containing 7·3 grams of th acid per litre neutralized 30 c.c. of caustic soda solution. 20 c.c. of this alka solution neutralized 20 c.c. of a solution of sulphuric acid. Calculate th normality and strength of sulphuric acid. *(Ajmer B.Sc. I Year 196*

Preparation of Standard Solution by Dilution

23. What volume of water must be added to 500 ml. of 1·56 N-sulphuri acid to make the solution exactly normal ? *(Senior Cambridge 1966 Jul*

24. 1·325 gm. of anhydrous sodium carbonate are dissolved in wate and the solution made up to 250 c.c. On titration 25 c.c. of this solutio neutralizes 20 c.c. of a solution of sulphuric acid. Calculate the normality o the acid. How much water should be added to 450 c.c. of this acid solution t make it exactly N/12 ? *(U.P. Board Inter. 196*

Based on Law on Equivalents

25. 55 c.c. of dilute hydrochloric acid are needed for complete decon position of 0·5 gm. of pure calcium carbonate. Calculate the normality of th acid. Find out the volume of carbon dioxide liberated in the reaction N.T.P. *(Punjab Inter. 196*

26. What weight of zinc carbonate can just neutralize 300 c.c. of 0·1 sulphuric acid ? (Zn=65) *(I.I.T. Admission Test 196*

Miscellaneous

27. What volume of N-HCl will be required to dissolve 0·25 gm. calcium carbonate ? What volume of CO_2 will be evolved at N.T.P. ?
(U.P. Board Inter. 196

28. 1·00 g. of a mixture of anhydrous sodium carbonate and potassiu carbonate was made up to 250 c.c. of aqueous solution. 25 c.c. of this solutic was neutralized by 20 c.c. of hydrochloric acid of unknown concentration. Th neutral solution then required 16·24 c.c. of 0·1 N-$AgNO_3$ for precipitation.

Calculate (i) the percentage by weight of K_2CO_3 in the mixture. (ii) th concentration of HCl, in grams per litre. *(I.I.T. Admission Test 196*

[Hint : 20 c.c. of N′-HCl≡16·24 c.c. of 0·1 N-$AgNO_3$. Knowing th normality of HCl, calculate normality of carbonate mixture. (It is=·065.)

Assuming it to be purely K_2CO_3 or purely Na_2CO_3, calculate the weights and use method of mixtures.]

29. 15 ml. of 12N-H_2SO_4 ; 30 ml. of 10N-HCl ; 10 ml. 2N-HNO_3 an 100 ml. of 3N-NaOH solution were mixed and the solution made up to 100 m Is the solution acidic or alkaline ? Express the acidity or alkalinity in terms normality ?
(Ajmer B.Sc. Ist Year 196

30. An acid (0·75 gm. ; mol. wt. 90) requires N-NaOH (16·8 ml.) fo neutralization. Calculate the basicity of the acid. *(Delhi Pre-Medical 196*

31. A sample of commercial hydrogen peroxide weighing 5·0 g. wa found to require 78·3 ml. of N-$KMnO_4$ for oxidation in the presence of aci What is the strength of hydrogen peroxide in weight percentage ?
(Delhi Pre-Medical 196

32. 10 c.c. of a mixture of H_2SO_4 and HCl solutions required 16 c.c. N/8 NaOH for exact neutralization.

20 c.c. of the same mixture when treated with excess of barium chlorid gave 0·3501 gm. of barium sulphate.

Calculate the amount of hydrochloric acid in one litre of the mixtur

33. Calculate the percentage of available chlorine in a given sample of bleaching powder from the following data :

3·55 gm. of the bleaching powder when treated with acetic acid and excess of potassium iodide liberated iodine which required 60 c.c. of 0·5 N-$Na_2S_2O_3$ solution. *(Bombay Inter. 1963 Supp.)*

34. Explain the terms with examples ;

Standard solution and Normal solution

25 ml. of a solution of containing 7·3 gm of the acid per litre neutralised 30 ml of NaOH. 20 ml of this alkali required 24 ml. of a solution of sulphuric acid for complete neutralisation. Calculate the normality and strength of sulphuric acid. *(Delhi H S. 1972)*

ANSWERS

2 (i) 1·47 gm. (ii) 1·26 gm
(iii) Anhydrous 4·5 gm., Crystals 6·3 gm.
(ii) (a) 31·6 gm ; (b) 49 gm. (c) 0·632 gm
(ii) H_2SO_4 = 36·75 gm. ; Na_2CO_3 = 39·75 gm. (iii) 58·5 gm.

3 (i) 1·0 (ii) 0·8 4 53·5 c.c. 5 27·17 litre.

6. 0·464 N ; 16·94 gm./litre 7 176·7 c.c.

8. 0·924 N ; 33·73 gm./litre. 9. Normality = 0·182.

10 0·139 ; 6·811 gm./litre 11 38·4

12 45. 13 150

14. 44·44% NaOH, 55·56% NaCl 15 8·33%

16 50%. 17 66% 18 90

19 2. 20. 75 21. 8

22. 0·167 ; 8·167 gm./litre 23 280 ml

24. 0·125 ; 225 c.c. 25. 0·182 ; 112 c.c.

26 1·875 gm. 27. HCl = 5 c.c., CO_2 = 56 c.c.

28. (i) 53·8% ; 2·37 gm./litre. 29. Acidic ; 0·2 N.

30 2. 31. 26·62%.

32 1·825 gm. 33. 30%.

34 Normality = 0·139 ; Strength = 0·139N or 6·836 gm./litre.

5. **Factors affecting the Rate of a Reaction.**—The rate at which a chemical reaction proceeds is referred to as the *rate of reaction or reaction velocity*. This is the rate at which a certain reactant changes or certain product is formed. The rate of a reaction depends upon several factors as given below :

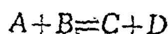
(*i*) **The nature of the reacting substances.** Hydrogen readily burns in oxygen forming water but under similar conditions the reaction between hydrogen and nitrogen is hardly perceptible. This shows that the rate of any reaction depends upon the nature of the reacting substances.

(*ii*) **Temperature.** A rise in temperature results in the increase of reaction velocity. It is approximately doubled with a 10°C rise in temperature. Thus a reaction which is completed in 8 hours at 10°C will require for completion only 4 hours at 20°C and only 2 hours at 30°C.

(*iii*) **Catalytic agents.** Decomposition of potassium chlorate is accelerated by the addition of manganese dioxide, which is found to have remained unchanged during the chemical reaction. Substances like manganese dioxide employed to accelerate the velocity of a chemical reaction are called **Catalytic agents.**

(*iv*) **Concentration or Pressure.** The effect of concentration or pressure on the rate of reaction is given by the Law of mass action. As stated by the Norwegian chemists, **Guldberg and Waage**, in 1884, the law states : "*The rate of a reaction is proportional to the molecular concentration of each of the reacting substances.*"

Molecular concentration or the *active mass* of a reactant or a product is the number of its gram molecules per unit volume and is represented by brackets. For example [*A*] stands for molecular concentration of *A*. Applying the law to a reversible reaction of the type



$$A+B \rightleftharpoons C+D$$

we have, Velocity of the forward reaction, $v_1 \propto [A] \times [B]$

or
$$v_1 = k_1 \times [A] \times [B]$$

Velocity of the backward reaction, $v_2 \propto [C] \times [D]$

or
$$v_2 = k_2 \times [C] \times [D]$$

where k_1 and k_2 are the constants of proportionality called the *velocity constants*. At equilibrium the rates of opposing reactions are equal, *i.e.*,

$$v_1 = v_2$$

or
$$k_1 \times [A] \times [B] = k_2 \times [C] \times [D]$$

or
$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K.$$

This is the mathematical form of the law of mass action. Since k_1 and k_2 are constants, the quotient k_1/k_2 is a constant quantity $= K$, which is called the *equilibrium constant*.

6. The Principle of Le Chatelier.—What happens when a system in equilibrium is subjected to a change of temperature, pressure and concentration, was first stated by Le Chatelier. According to him, "*If a system in equilibrium be subjected to a change of temperature, pressure or concentration, the equilibrium will shift in a direction which tends to undo the effect of change impressed.*"

This is known after his name as **Le Chatelier's Principle** and is used to predict the effect of change of temperature, pressure and concentration on a system in equilibrium.

To understand the principle, let us predict the effect of change of these factors on a few systems in equilibrium.



Henry Le Chatelier
(1850—1936)
French chemist who was Professor of Chemistry in Paris. In 1883, he stated the famous principle known after his name

(i) Ice ⇌ Water − Heat

The change from ice to water is reversible, endothermic and proceeds with decrease in volume.

Effect of Change in Pressure

When we *increase the pressure*, the system tends to decrease its volume in order to relieve the excess of pressure (undo the effect of change). Thus the equilibrium shifts forward—a direction which is accompanied by decrease in volume, *i.e.*, some of the ice melts.

Effect of change in Temperature. Now if we *heat the system*, the system tends to shift its equilibrium in a direction which is accompanied by the absorption of heat in order to keep its temperature unchanged, *i.e.*, forward. Thus some of the ice melts and absorbs the heat supplied to the system.

(ii) $N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22{,}400$ cal.

The forward reaction is reversible, exothermic and is accompanied by decrease in volume.

Effect of change in Temperature. When we heat the system, the equilibrium shifts in a direction accompanied by absorption of heat, *i.e.*, backward.

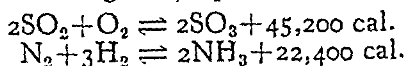
Effect of change in Pressure. When the pressure on the system is increased, the equilibrium shifts in a direction accompanied by decrease in volume which results in relieving of pressure, *i.e.*, forward.

Effect of change in Concentration. An addition of nitrogen results in increase of its concentration. The system tends to bring its concentration to the original level by making some hydrogen, react with it to form ammonia. This results in shifting of the equilibrium forward.

Thus favourable conditions for better yield of ammonia are: (i) Low temperature, (ii) High pressure, and (iii) Excess of nitrogen or hydrogen.

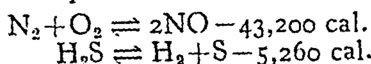
For application of Le Chatelier's principle to a few more systems in equilibrium refer to manufacture of sulphuric acid and nitric acid by Contact Process and Birkland Eyde Process respectively.

To summarise 1. Exothermic reversible reactions are more nearly complete at lower temperatures while endothermic ones are more nearly complete at higher temperatures. For example:



$$2SO_2+O_2 \rightleftharpoons 2SO_3+45{,}200 \text{ cal.}$$
$$N_2+3H_2 \rightleftharpoons 2NH_3+22{,}400 \text{ cal.}$$

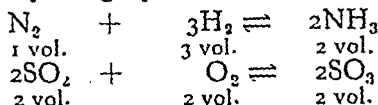
are favoured by a low temperature.



$$N_2+O_2 \rightleftharpoons 2NO-43{,}200 \text{ cal.}$$
$$H_2S \rightleftharpoons H_2+S-5{,}260 \text{ cal.}$$

are favoured by an increase in temperature.

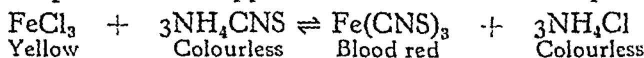
2. A reaction which is accompanied by a decrease in volume is favoured by a high pressure. For example:



$$\underset{1 \text{ vol.}}{N_2} + \underset{3 \text{ vol.}}{3H_2} \rightleftharpoons \underset{2 \text{ vol.}}{2NH_3}$$
$$\underset{2 \text{ vol.}}{2SO_2} + \underset{2 \text{ vol.}}{O_2} \rightleftharpoons \underset{2 \text{ vol.}}{2SO_3}$$

are favoured by high pressure.

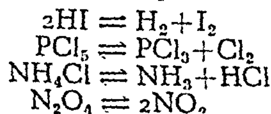
3. An increase in concentration of any one of the constituents shifts the equilibrium in opposite direction. For example:



$$\underset{\text{Yellow}}{FeCl_3} + \underset{\text{Colourless}}{3NH_4CNS} \rightleftharpoons \underset{\text{Blood red}}{Fe(CNS)_3} + \underset{\text{Colourless}}{3NH_4Cl}$$

An increase in the concentration of $FeCl_3$ shifts the equilibrium forward resulting in the formation of more of the red $Fe(CNS)_3$—*the colour deepens.* On the other hand, increase in the concentration of NH_4Cl shifts the equilibrium backward resulting in the formation of more of colourless NH_4CNS and yellow $FeCl_3$—*the red colour fades.*

7. **Thermal Dissociation.**—Certain substances like hydriodic acid, ammonium chloride, etc. are found on heating to split up into simpler molecules which reunite on cooling to give the original substances. The process is called *Thermal Dissociation.* It can be defined as *the process of decomposition of certain substances on heating into simpler molecules which recombine on cooling to give the original molecules.* It differs from simple decomposition in being *reversible.* A few examples of thermal dissociation are:



$$2HI \rightleftharpoons H_2+I_2$$
$$PCl_5 \rightleftharpoons PCl_3+Cl_2$$
$$NH_4Cl \rightleftharpoons NH_3+HCl$$
$$N_2O_4 \rightleftharpoons 2NO_2$$

The *degree of dissociation* is the extent to which dissociation occurs. The vapour density of a gas decreases as dissociation proceeds and the vapour density at a certain temperature is a measure of dissociation at that temperature.

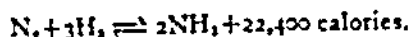
QUESTIONS

Essay-type Questions

1. Write a short note on 'Equilibrium'. (Punjab Pre-Medical/Pre-Engg /T.D.C. (I) 1969)

2. State and explain the Law of mass action.

Discuss the effect of temperature and *pressure* on the following equilibrium :



$$N_2+3H_2 \rightleftharpoons 2NH_3+22{,}400 \text{ calories.}$$

State the effect of adding ammonia to the system. (Madhya Pradesh Inter. 1964)

3. State Le Chatelier's law and give examples where the law is applied to chemical processes. (Nagpur Pre-Univ. 1970 ; Delhi Pre-Medical 1961)

4. Write short notes on :
(a) Gaseous Dissociation. (b) Thermal Dissociation.

5. Explain what do you understand by Reversible reaction (Punjab Pre-Medical/Pre-Engg /T.D C. (I) 1969 , U.P. Inter. 1961)

6. A chemical reaction is slow. *How can you increase its speed* ? Give one example of each of the factors you suggest. (Bihar H.S. 1962 Supp)

7. (a) *What do you understand by* Equilibrium constant of a chemical reaction ?

(b) State Le-Chatelier principle. How would you apply it to determine the effect of (i) increase of pressure and (ii) increase of temperature of the following exothermic reaction ? $2SO_2+O_2 \rightleftharpoons 2SO_3$ (Delhi Pre-Medical 1972)

Test Your Understanding :

8. *Fill in the blanks in the following :*

(a) The rate of a reaction is proportional to the of each of the reacting substances.

(b) At the point where the two opposing reactions are going on at the same time and with the same rate, there is a state of . or

(c) .. . or active mass of A is its number of per and is represented by .....

(d) The favourable condition for better yield of ammonia in the reaction $N_2+3H_2 \rightleftharpoons 2NH_3+22{,}400$ cal

are (i) . .. , (ii) . . , and (iii)

(e) Process of decomposition of certain substances on heating into simpler molecules which recombine on cooling to give the original molecules, is termed. . .

KEY

(a) molecular concentration ; (b) balanced activity, chemical equilibrium ; (c) molecular concentration, gram molecules, unit volume, [A] , (d) low temperature, high pressure, excess of nitrogen, or hydrogen ; (e) thermal dissociation.

SOLUTION IS A HOMOGENEOUS MIXTURE, THE PROPORTION OF WHOSE CONSTITUENTS CAN VARY WITHIN CERTAIN LIMITS.

FORMALITY = No. OF Gm. FORMULA Wt./l
NORMALITY = " " " EQUIVALENT "/l
MOLARITY = " " MOLES/l
MOLALITY = No. OF MOLES PER 1000 gm OF SOLVANT

Solution

1. **What Solution is ?**—When we add a spoonful of sugar to some water in a cup, sugar gradually disappears. Sugar is said to have dissolved in water to form a uniform mixture from which sugar can be re-obtained by evaporation. A teaspoonful of sugured water from the top of the cup is as sweet as a teaspoonful from the middle or bottom of the cup. This shows that sugar dissolves in water to form a homogeneous mixture in which the quantity of sugar to be added can be varied within certain limits. The homogeneous mixture of sugar and water so obtained is termed a solution.

Thus **solution** *may be defined as a homogeneous mixture, the proportion of whose constituents can vary within certain limits.*

2. **Solvent and Solute.**—Every solution is made up of at least two constituents. One of the constituents (say, *A*) dissolves the other (say, *B*) and so forms a continuous medium surrounding the dispersed molecules of the other constituent, *B*. Here *A*, *the constituent that forms the continuous medium, is termed the* **solvent** *while B, the constituent that is dissolved or dispersed, is called the* **solute**.

A solution with water as solvent is known as aqueous solution while a solution in which the solvent is alcohol is called alcoholic solution. In a solution containing 80% water and 20% alcohol, water is the solvent while alcohol is the solute. In another sample containing 20% water and 80% alcohol, the solvent is alcohol while the solute is water.

3. **Types of Solution.**—Constituents of a solution may be solids, liquids or gases. Solutions may, therefore, exist in the liquid, solid or gaseous state. Different types of solution as judged by the state of their constituents are :

(i) Solid in Liquid, *e.g.*, sugar in water or salt in water.

(ii) LIQUID IN LIQUID, *e.g.*, alchohol in water or alcohol in ether. Two liquids which are soluble in each other are called *miscible* while others like oil and water which are not soluble in each other are called *immiscible*. *A suspension of one liquid in another liquid is called an* emulsion, *e.g.*, fresh milk is an emulsion of fat globules in water containing casein and milk sugar.

(iii) GAS IN LIQUID, *e.g.*, oxygen dissolved in water or aerated water, a solution of carbon dioxide in water.

(iv) SOLID IN SOLID, *e.g.*, brass, a solution of zinc in copper; gold dissolved in lead.

(v) LIQUID IN SOLID, *e.g.*, mercury dissolved in copper.

(vi) GAS IN SOLID, *e.g.*, palladium or platinum dissolves on heating fairly large quantities of hydrogen. *This phenomenon of dissolution of gases in solids is called* occlusion.

(vii) GAS IN GAS, e.g., air or any other mixture of gases.

4. **Process of Dissolution.**—Electrovalent compounds dissolve in polar solvents like water. During the process of dissolution they split up into ions which are then hydrated. For example, sodium chloride molecules on dissolution in water split up into Na^+ and Cl^- which attract water molecules and get hydrated.

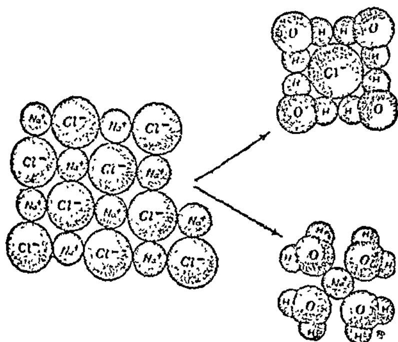


Fig. 20·1—Schematic representation of the dissolution of sodium chloride in water. Slightly positively charged hydrogen atoms of the polar water molecules are attracted by the Cl^- ions whereas the negatively charged oxygen atoms are drawn towards the Na^+ ions

Covalent compounds like sugar when dissolved in water do not split up into ions. The molecules retain their identity but these are heavily hydrated. Thus each sugar molecule is surrounded by a cluster of water molecules (Fig. 20·2).

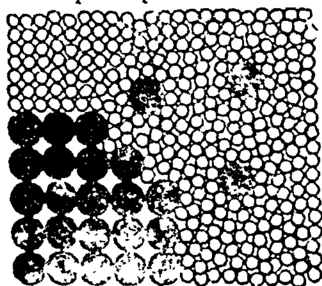


Fig. 20·2—Schematic representation of the dissolution of sugar in water.

5. Methods of expressing Concentrations.—A solution, containing a relatively small quantity of the solute, is called a *dilute solution*. On the other hand, a solution is said to be *concentrated* if the relative quantity of the solute is large.

The terms *dilute* and *concentrated* like the words *little* and *much* are rather indefinite and lack the definiteness or precision needed in the study of science. Concentrations of solutions may be more accurately expressed in physical or chemical units, e.g., weight ratio—weight of solute per unit volume of solution. *A solution of known concentration is called a* **standard solution.**

Different terms commonly used for expressing the concentrations of solutions are :

(1) **Molarity.** *Number of moles of the solute present per litre of the solution is termed* **Molarity** *of the solution.* It is denoted by *M*.

For example, molecular weight of sodium carbonate is 106 and one mole of Na_2CO_3 = 106 gm. A solution containing 53 gm. of sodium carbonate dissolved in one litre of the solution contains 0·5 mole of Na_2CO_3 per litre.

∴ Molarity of this solution

$$=0{\cdot}5 \text{ or it is } 0{\cdot}5\ M\text{-}Na_2CO_3.$$

In general, molarity of a solution

$$=\frac{\text{Grams of solute per litre of solution}}{\text{Gram molecular weight of solute}}$$

(2) **Formality.** Substances like sodium chloride exist as giant molecules in which each Na^+ ion is surrounded by 6 Cl^- ions and each Cl^- ion is surrounded by 6 Na^+ ions. Substances like hydrofluoric acid exist as associated molecules, $(HF)_2$. In their case it would not be correct to use the term molecular weight. Pauling has used the term formality for expressing their concentration. *Formality of a solution is the number of gram formula weights dissolved per litre of the solution.*

Formality of a solution containing 11·7 gm. of sodium chloride (formula weight=58·5)$=\frac{11 \cdot 7}{58 \cdot 5}=0 \cdot 2$.

Or the strength of the solution

=0·2 formal (=0·2 *F*)

(3) **Normality.** *Number of gram equivalent weights of a solute dissolved per litre of solution is termed its* **normality.**

$$\text{Normality}=\frac{\text{Strength in grams/litre}}{\text{Gm. eq. wt}}$$

For example, normality of a solution containing 5 gm. of NaOH (Eq. wt.=40) per litre$=\frac{5}{40}=0 \cdot 125$.

(4) **Molality** *Number of moles of the solute per 1000 grams of the solvent is termed* **Molality** *of the solution.* It is denoted by *m*.

For example, 1 molal (1·0 *m*) aqueous solution of caustic soda (mol. wt.=40) is prepared by dissolving 40 gm. of it in 1000 gm. of water.

(5) **Mole fraction** *The fraction obtained by dividing the moles of the constituent A by the total number of molecules (of A and B combined) is termed* **mole fraction** *of A.* It is denoted by X_A.

$$\therefore \text{Mole fraction of A, } X_A=\frac{\text{No. of moles of A}(n_A)}{\text{No. of moles of A}(n_A)\text{ and of B}(n_B)}$$

$$=\frac{n}{n_A+n_B}$$

Similarly mole fraction of B, $X_B=\frac{n_B}{n_A+n_B}$

(6) **Weight per cent.** *Weight of solute in grams present in 100 grams of solution is termed* **weight per cent.** For example, strength of a solution containing 5 gm. of caustic soda in 35 gm. of water

$$=\frac{\text{Wt. of solute}}{\text{Wt. of solution}}\times 100$$

$$=\frac{\text{Wt. of solute}}{\text{Wt. of solute + wt. of solvent}}\times 100$$

$$=\frac{5}{5+35}\times 100=12 \cdot 5\% \text{ by weight.}$$

Example. *Calculate the weights of the solute present in each of the following solutions :*

(*a*) *1 litre of 0·8 F-NaCl ;*

(*b*) *2 litres of 0·6 M-Na_2CO_3 ;*

(*c*) *500 ml. of 2N-KOH ;*

(*d*) *1040 gm. of 1 m-NaOH ;*

(*e*) *63 gm. of 5% by weight of copper sulphate.*

(*a*) Wt. of solute in 1 litre of 0·8 F-NaCl (formula weight $=58{\cdot}5)=58{\cdot}5\times0{\cdot}8=46{\cdot}8$ gm.

(*b*) Wt. of Na_2CO_3 (Mol. wt.$=106$) in 2 litres of 0·6 M-$Na_2CO_3=2\times106\times0{\cdot}6$

$=127{\cdot}2$ gm.

(*c*) Wt. of KOH (Eq. wt.$=56$) in 500 ml. of 2N=KOH.

$$=56\times2\times\frac{500}{1000}=56 \text{ gm.}$$

(*d*) 1 *m*-NaOH contains 1 mole of NaOH($=40$ gm.) in 1000 gm. of water or $40+1000=1040$ gm. of solution.

∴ Wt. of NaOH in 1040 gm. of 1 *m*-NaOH$=40$ gm.

(*e*) 100 gm. of 5% copper sulphate solution contain 5 gm. of copper sulphate.

∴ Wt. of copper sulphate in 63 gm. of solution

$$=\frac{63}{100}\times5=3{\cdot}15 \text{ gm.}$$

6. **Unsaturated, Saturated and Supersaturated solutions.**—When a cube of sugar is added to a cup of tea, it dissolves. If this process of addition of sugar cubes is continued, a limit is reached when the last sugar cube does not dissolve. *The solution so obtained in which no more sugar can be made to dissolve, except by raising the temperature, is called a* **saturated solution.**

Previous to this stage of saturation when the solution could dissolve more and more of the solute, it was an unsaturated solution. **An unsaturated solution** *is one that can dissolve more of the solute at that temperature.*

When a saturated solution is filtered and allowed to stand undisturbed, it will often retain on cooling all the extra solute that it previously dissolved. The solution so obtained is termed a **supersaturated solution.** It contains more dissolved solute than could be present in its saturated solution. It is only an abnormal condition and on slight disturbance or on the addition of a crystal, the excess of the solid separates as crystals.

For testing whether the solution is saturated, unsaturated or supersaturated, add an extra crystal of the solute to it.

(*a*) The solution is dilute if the crystal dissolves.

(*b*) It is saturated if the crystal remains unchanged.

(*c*) The solution is supersaturated if the crystal added induces crystallization.

7. **Solubility and its Determination.**—Some substances dissolve readily in water while some others are almost insoluble. Substances which are insoluble in water dissolve in some other solvent. Thus different substances differ greatly in their solubility behaviour.

The solubility of solid depends upon three factors, *viz.*, (i) nature of the solid ; (ii) nature of the solvent used ; and (iii) the temperature. Hence while expressing solubility of a substance, the nature of the solvent and the temperature must be clearly stated. It is commonly defined in three different ways as given below :

Solubility of a substance is the maximum weight of it in grams which will dissolve in 100 grams of the solvent at a given temperature.

or

Solubility of a substance is its weight in grams present in 100 c.c. of its saturated solution at a given temperature.

or

Solubility of a substance is its weight in grams present in 100 grams of its saturated solution at a given temperature.

For experimental determination of solubility we proceed as given in the experiment as given below .

Expt. 1. Take 30–40 ml of water in a beaker and just warm it a little. Add a little of the well-powdered substance whose solubility is to be determined. Stir with a clean rod If it dissolves, go on adding more and more of solid and stirring till some powder settles down and does not go in solution. This is the saturated solution.

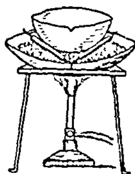


Fig 20 3—Evaporation of the solution.

Now weigh a clean evaporating dish. Note the [illegible]

[illegible] when most of the water gets evaporated. So at that time, be very careful to use a low flame. When whole of water has evaporated and only last traces of it are left, a hissing sound is produced and continues till there is no moisture left. Now heat it a little more. Cool it in a desiccator and weigh to a constant weight.

Observations and Calculations :

Temperature of the room	$=t°C$
Wt. of china dish	$=x$ gm.
Wt. of china dish+solution	$=y$ gm.
Wt. of solution taken	$=(y-x)$ gm.
Wt. of dish+residue left (i)	$=z$ gm.
(ii)	$=z$ gm.
Wt. of residue left	$=(z-x)$ gm.
Wt. of water evaporated	$=(y-z)$ gm.
Hence solubility	$=\frac{z-x}{y-x}\times 100$ gm. per 100 gm of water.

Example. *10·5 gm. of a saturated solution of potassium chloride at 40°C contains 3 gm. of the salt. Calculate the solubility of potassium chloride at 40°C.* (Senior Cambridge 1967 Nov.)

Wt. of the saturated solution = 10·5 gm.

Wt. of the salt contained = 3·0 gm.

Wt. of water = 10·5 − 3·0
= 7·5 gm.

7·5 gm. of water dissolved 3·0 gm. of the salt at 40°C

Wt. of the salt dissolved by 100 gm. of water

$$= \frac{3}{7 \cdot 5} \times 100 = 40 \text{ gm.}$$

Solubility of potassium chloride at 40°C

= 40 gm. per 100 gm. of water

10·5 gm. of saturated solution contains 3 gm. of the salt at 40°C.

100 gm. of the saturated solution will contain salt

$$= \frac{3}{10 \cdot 5} \times 100 = 28 \cdot 57 \text{ gm.}$$

i.e., Solubility of potassium chloride at 40°C

= 28·57 gm. per 100 gm. of its saturated solution in water

8. **Solubility Curves.**—Generally the solubility of a substance increases with the rise of temperature. The increase being rapid in certain cases, *e.g.*, potassium nitrate, and very slow in other cases, *e.g.*, sodium chloride, it actually decreases in a few cases, like lime, calcium sulphate and anhydrous sodium sulphate. The graph drawn for change of solubility of a substance with rise of temperature is called a **solubility curve.**

To draw solubility curves, temperature is represented along the abscissa and solubility along the ordinate. The points plotted are joined by a smooth curve which gives us a solubility curve as shown in Fig. 20·4.

Uses of Solubility Curves. (*i*) Solubility of a given salt at a given temperature can be directly read from its solubility curve.

(*ii*) Their shape gives the change of solubility with temperature at a glance. A steep curve shows that change is rapid and a flat curve shows that the change is slow.

(*iii*) A sharp break in the solubility curve shows a *transition temperature*, *e.g.*, in sodium sulphate curve below 32·5°C $Na_2SO_4 \cdot 10H_2O$ crystallizes out while above it Na_2SO_4 crystallizes

9. **Solubility of Gases.**—The solubility of a gas varies with the nature of the gas and is found to decrease with rise in temperature (*c.f.* solubility of a solid which generally increases with an increase in temperature). Pressure also affects the solubility of gases as given by Henry's law which states *that the amount of a gas absorbed by liquid is directly proportional to the pressure of the gas.* The law does not apply to gases which are very soluble, *e.g.*, carbon dioxide or ammonia or others which enter into chemical combination with the solvent, *e.g.*, sulphur dioxide which dissolves in water to give sulphurous acid, H_2SO_3.

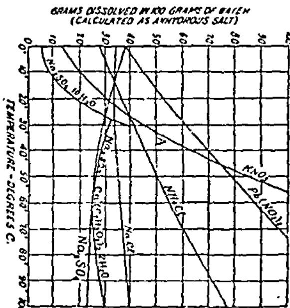


Fig 20 4—Solubility curves.

SOME MODERN CONCEPTS

10. **Why Substances Dissolve ?**—Every system has two tendencies, (*a*) to have as little energy as possible or to *move towards decrease in energy*, and (*b*) to have as much *randomness* or *disorganisation* as possible or to *move towards increased randomness.*

(*a*) **Decrease in Energy.** When sodium chloride is dissolved in water, the solution is found to be cooler than the water [illegible] water during the [illegible] dissolved mole[illegible] ones. *There is a greater tendency towards precipitation than towards solution due to the energy effect.*

(*b*) **Increase in Randomness or Entropy.** Molecules are more closely packed in the solid and the liquid states while they are freer to move in the gaseous state. We say they have more *randomness* in the gaseous state, or their movements are less restricted.

Systems tend to move from a state of lesser randomness, to a state of greater randomness, *i.e.*, from an organised to a disorganised state. In solid sodium chloride, the particles constituting it have fixed positions, in solution they have greater freedom of movement. Solution represents a state of greater randomness. Hence *randomness favours solution.*

Thus there are two *opposing* factors in the dissolution of a substance: randomness trying to increase the solubility while energy factor trying to decrease it. If the former factor prevails, the substance dissolves, if the latter prevails it does not dissolve.

11. Temperature and Solubility.—Temperature always increases *randomness*, the molecules get more energy and hence have greater freedom of movement. Hence *due to increased randomness solubility increases with rise in temperature.*

Most of the solids dissolve in liquids, absorbing heat



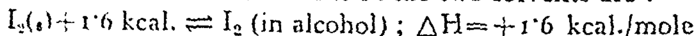
$$\text{solid} + \text{heat} \overset{\text{solvent}}{\rightleftharpoons} \text{solution}$$

Applying Le Chatelier's principle we find that increase of temperature will favour solution from the consideration of heat effects. The change of heat content during solution is termed *heat of solution. The change of heat content when one mole of a substance dissolves is its heat of solution.* The heat of solution, ΔH, in the above example is *positive*. Hence a positive change of heat content favours solubility with increase in temperature while a negative change of heat content favours precipitation (decreased solubility) with increase in temperature.

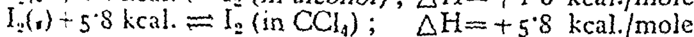
12. Why does a Substance have Different Solubilities in Different Solvents?—Iodine is soluble both in alcohol and in carbon tetrachloride. However, its solubility in the former is 0·84 mole/litre while in the latter it is only 0·12 mole/litre at room temperature. Why is it so?

It has been stated above that at the same temperature, solubility of a substance is determined by (*i*) randomness effect, (*ii*) energy effect. In the above case the randomness effect is the same in both cases—iodine molecules regularly arranged in the crystal change to the disordered form in solution. What about the energy effect?

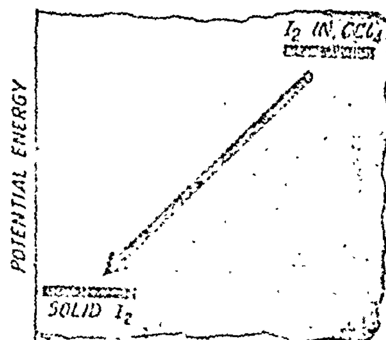
The heats of solution of iodine in the two solvents are :



$$I_2(s) + 1{\cdot}6 \text{ kcal.} \rightleftharpoons I_2 \text{ (in alcohol)}; \quad \Delta H = +1{\cdot}6 \text{ kcal./mole}$$



$$I_2(s) + 5{\cdot}8 \text{ kcal.} \rightleftharpoons I_2 \text{ (in } CCl_4\text{)}; \quad \Delta H = +5{\cdot}8 \text{ kcal./mole}$$



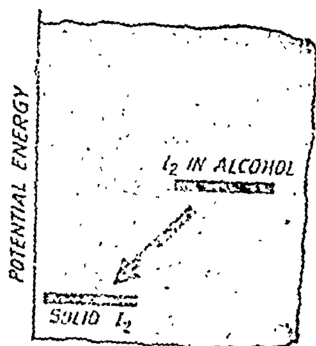


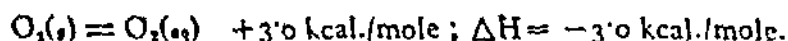
Fig. 20·5—A large energy difference between solid and solution lowers the solubility.

larger for carbon tetrachloride than for alcohol. Hence the solubility of iodine in carbon tetrachloride is much less than in alcohol.

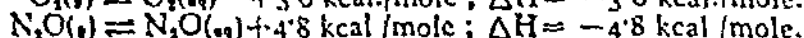
13. **Solubility of Gases in Liquids.**—The principles governing solubility can be applied to an equilibrium of a gas-liquid system—the movement of a system to *maximum randomness and minimum energy.*

(*a*) Maximum randomness. There is greater freedom of movement for the molecules in the gaseous phase than in solution. *Hence randomness effect favours the gas phases and opposes its solubility.* This is just reverse of what we saw in the case of solids.

nearer one another. Their increased attraction for one another (at shorter distances) *lowers the potential energy of the system.* So when gas dissolves in a liquid, *heat is evolved*, as the system possesses lesser energy. Thus energy considerations favour the dissolution of gases. This is again in contrast to what we found in a solid-liquid system. It means the greater the heat effect (*more negative it is*), the greater the solubility of the gas (provided randomness factor is the same). Consider the heats of solution of following two gases :



$$O_2(g) \rightleftharpoons O_2(aq) \quad +3{\cdot}0 \text{ kcal./mole} ; \ \Delta H = -3{\cdot}0 \text{ kcal./mole.}$$



$$N_2O(g) \rightleftharpoons N_2O(aq) + 4{\cdot}8 \text{ kcal /mole} ; \ \Delta H = -4{\cdot}8 \text{ kcal /mole.}$$

The heat of solution of nitrous oxide is more negative than that of oxygen ; its solubility is greater than that of oxygen.

When temperature is increased, the random state is favoured. Increased randomness in gas-liquid systems means lower solubility of the gas. *Hence the solubility of a gas decreases as temperature increases.*

14. [illegible] aturated solution of a solid [illegible] *particles having regular ge*[illegible] orms eight-sided or *octahedral* crystals and copper sulphate deposits *rhombohedral* crystals that are blue in colour. *The process of deposition of crystals of a salt from its concentrated solution is called crystallization.* Chemists purify chemicals by crystallization while definite shape of the crystals helps *in their identification* in crystallography. Diamonds and the tiny crystals used in your radio receiving set (crystal set) are only natural crystals.

15. **Water of Crystallization.**—During the process of crystallization, many crystals, although not all, crystallize out as hydrates containing definite amounts of water. The water they contain is called *water of hydration* or *water of crystallization.* A few common examples of salts containing water of crystallization are : $CuSO_4.5H_2O$, $Na_2SO_4.10H_2O$, $ZnSO_4.7H_2O$. Crystalline shape of these hydrated crystals and very often their colour is due to their water of crystallization. For example, on heating $ZnSO_4.7H_2O$ crystals, these crumble to a powder while $CuSO_4.5H_2O$ crystals on heating lose their blue colour and yield a white powder. The blue colour is regained on moistening the white residue with water.

The water of crystallization in a given substance can be estimated by heating a known weight of the crystals in a dish at 100°C. The loss in weight gives the water of crystallization lost. In some cases, however, the whole of the water of crystallization may not be expelled at 100°C, *e.g.*, $CuSO_4.5H_2O$, loses only four molecules of water at 100°C.

16. **Efflorescence.**—Certain hydrated salts like washing soda ($Na_2CO_3.10H_2O$) and Glauber's salt ($Na_2SO_4.10H_2O$) lose their water of crystallization and crumble to powder when exposed to air. These substances are called *efflorescent* while the phenomenon is called *efflorescence.* A hydrated salt will effloresce only if its vapour pressure is higher than the partial pressure of the water vapour in air.

17. **Deliquescence.**—Certain other substances like calcium chloride, zinc chloride absorb moisture when exposed to air and finally pass into solution. Such substances are called *deliquescent* and the phenomenon is called *deliquscence.* Absorption of moisture is due the fact that vapour pressure of deliquescent substances is less than the partial pressure of water vapour present in air.

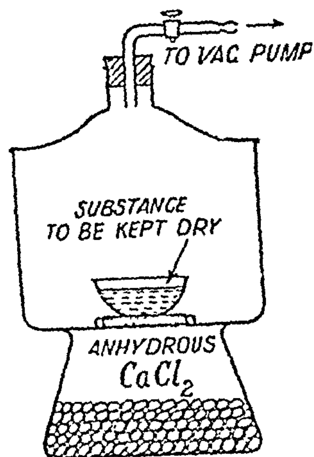


Fig. 20·6—A desiccator.

Being deliquescent calcium chloride is used as a valuable desiccating agent. A desiccator (Fig. 20·6) is used in the laboratory for drying substances or keeping them away from moisture. The lower part of the desiccator is filled with calcium chloride which absorbs moisture of the air present inside. Thus the substance present inside is always surrounded by dry air and even loses its own moisture, if any.

18. **Hygroscopic Substances.**—Many substances like silk wool and tobacco are found to absorb moisture from the air. They are said to be hygroscopic (*Greek—to seize water*). Sodium chloride crystals always contain a small amount of magnesium chlorid

as impurity and as a result has a slight tendency to pick up moisture. It is a hygroscopic substance. Magnesium chloride which [illegible]

so as to become wet.

QUESTIONS

Essay-type Questions :

1. Explain the meaning of the following terms :

(a) Solution, (b) Supersaturated solution, (c) Sublimation, (d) Solubility of a substance, and (e) Solubility curve.

How are solubility curves drawn and what is their use ?

2. Write short notes on

(i) "Efflorescence and Deliquescence" giving examples.

(ii) Molarity and molality *(Punjab Pre-Univ. 1970)*

(iii) Formality and mole fraction.

3. (a) What do you understand by solubility ? How is this property of matter affected by a rise in temperature ? *(Delhi H.S 1969)*

(b) What are saturated and supersaturated solutions ? *(Delhi H.S. 1968)*

4. How does the modern chemist explain the following :

(a) Why substances dissolve ?

(b) Effect of temperature on solubility.

(c) Why does a substance have different solubilities in different solvents ?

(d) Solubility of gases in liquids

5. 100 grams of water at 15°C dissolve at saturation 37 gm. of sodium chloride and 25 gm. of potassium nitrate but at 70°C, the corresponding weights are 38 gm. and 140 gm. per 100 gm of water respectively.

[illegible] portions by [illegible] is reached. [illegible] °C and again [illegible]

What will be the weights and composition of the three residues, assuming that no solution is left in either of the filter papers ? *(Senior Cambridge 1965 July)*

6. The solubility of sodium chloride at t°C is 36 gm. of the anhydrous [illegible] evaporating [illegible] would be [illegible] gm. of the [illegible] solution. *(Senior Cambridge 1962 Nov.)*

7. 12·0 gm. of a solution of potassium nitrate saturated at 15°C left on evaporation 2·40 gm. of potassium nitrate. Calculate and quote correctly the solubility of potassium nitrate at 15°C. *(Senior Cambridge 1962 July)*

8. (a) Why do many inorganic compounds dissolve in water ?

(b) Describe the following :—

(i) Solubility of a substance ; (ii) Deliquescence ; (iii) Supersaturated solution.

Test Your Understanding

9. Fill in the blanks in the following :

(i) Solution is a......mixture, the proportions of whose constituents can......within certain limits.

(ii) In a solution the constituent that forms the continuous medium is termed the......while the constituent which is dissolved or dispersed is called......

(iii) The solubility of a......in a......at a particular temperature is the number of grams of solute required to......100 grams of solvent at that temperature.

(iv) When sodium chloride dissolves in water, the solution is found to be cooler. Hence the dissolved molecules have......energy (enthalpy) and......randomness (entropy).

(v) When a gas is dissolved in water, its enthalpy......and entropy....

(vi) Solubility of a gas......as temperature increases.

10. Which of the statements given below is correct in the case of a solution of sodium hydroxide ?

(i) formality = molarity

(ii) normality = formality

(iii) molarity = normality.

KEY

9. (i) homogeneous, vary ; (ii) solvent, solute ; (iii) solute, solvent, saturate ; (iv) higher, greater ; (v) increases, decreases ; (vi) decreases.

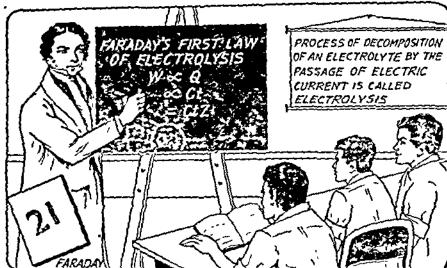
10. (ii).

ANSWERS

5. (i) 12 gm. NaCl ; (ii) 1 gm. NaCl and 25 gm. KNO_3 ; (iii) 37 gm. NaCl and 25 gm. KNO_3.

6. 26·47 gm. ; 32·45 gm.

7. 25 gm. per 100 gm. of water at 16°C.



Electrolysis

1. Electrolytes and non-electrolytes.—A substance which ɔws an electric current to flow through it is called a **Conductor** ile another which does not allow any electric current to flow ough it is called an **Insulator**. Conductors are of two kinds: *Metallic conductors* which remain unchanged as current flows ough them; (ii) Solutions of salts like sodium chloride which decomposed by the passage of the electric current.

Substances of the later type whose water solutions conduct the *ctric current and which are decomposed by the passage of electric* *rrent are called* **Electrolytes.**

A compound whose aqueous solution does not conduct electric *rent is called* **Non-electrolyte.** Solutions of cane-sugar, glyce-ie and alcohol do not ıduct electricity and examples of non-ctrolytes.

Expt. 1. Connect an ctric lamp in series with platinum wires or plates ch dip into a solution con-ned in a battery pot. nnect it further to the ctric mains through a plug shown in Fig. 21·1.

Put the solution of an ctrolyte in the battery pot d switch on the current. e lamp filament begins to w showing that the electro-es conduct electric current. w place the solution of ne non-electrolyte or pure water in the battery pot and switch on the rrent. The lamp filament will not glow, illustrating thereby that the non-ctrolytes do not conduct electric current and that pure water is a non-ctrolyte.

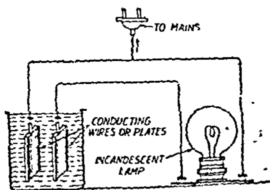


Fig. 21·1—Electrolytes conduct electric current, non-electrolytes do not.

A metallic conductor behaves as if it contains electrons which are relatively free to move. An electric current flows through the metallic conductors as a result of the flow of electrons. The passage of current through such a conductor has no observable effect other than that of raising its temperature. An electrolyte in its fused state or its aqueous solution contains no detectable concentration of electrons. It conducts electricity not by virtue of the flow of electrons but as a result of the movement of ions which are electrically charged. When current traverses the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from an ion. Removal of electrons from atoms, molecules or ions is termed *oxidation* (*de-electronation*) while addition of electrons to atoms, radicals or ions is called *reduction* (*Electronation*). ence flow of electrons across the boundary is accompanied by oxidation or reduction.

Conduction of current through a metallic conductor and an electrolytic conductor may be briefly distinguished as below:

Metallic conduction	*Electrolytic conduction*
1. It consists of the flow of electrons in the conductor.	1. It consists of the movement of ions in solution or a fused electrolyte.
2. It involves no change in the chemical properties of the conductor.	2. It involves chemical reactions which take place at electrodes (see electrolysis below).
3. It does not involve the transfer of any matter.	3. It involves transfer of matter in the form of ions.
4. It generally shows increase in resistance as temperature is increased.	4. It generally shows a decrease in resistance as the temperature is increased because the viscosity of the medium and the degree of hydration of the ions decreases with increasing temperature.

2. **Electrolysis.**—*The process of decomposition of an electrolyte by passage of electric current through it is called* electrolysis. To bring about the electrolysis of a solution, we are required to dip two metallic rods or plates in the solution and connect them by means of a wire to the two terminals of a battery. These metallic rods or plates which lead the electric current to and from the electrolyte are termed **Electrodes.** The electrode connected with the positive pole of the battery is called the *positive electrode* or the **Anode** while the other connected with the negative pole of the battery is called the *negative electrode* or the **Cathode.** The current enters the electrolyte through the anode and leaves through the cathode.

Molecules of an electrolyte when dissolved in water split up into negatively and positively charged particles called **Ions** while

the process of splitting up of the molecules is called [illegible].* On electrolysis, positively charged ions move towards the [illegible] and are called Cations. The negatively charged ions which move towards the anode are called Anions.

At the cathode positively charged ions (cations) [illegible] electrons and are thereby reduced. At the anode negatively charged ions (anions) lose electrons and are, therefore, oxidised.

The study of solutions of electrolytes and of the [illegible] occurring at *electrodes* [illegible] Electro-chemistry. It is [illegible] stry emerged as a distinct science [illegible].

3. **Conductance of Solutions.**—[illegible] lyte is due to the presence of these ions.

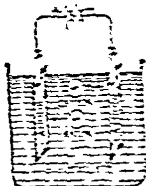


Fig. [illegible]

It depends on:

(i) the number of ions per unit volume,

(ii) the charge on the ions, and

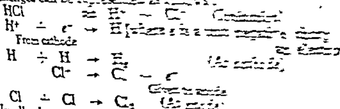
(iii) the speed with which the ions move.

(*a*) **On dilution**, the total number of ions in a weak electrolyte increases but the number of ions per unit volume decreases. As a result of it, the conductance decreases.

(*b*) **On heating**, the viscosity of the solution is lowered and thus the speed of the ions increases. Consequently the conductance of the solution increases.

(*c*) **On melting**, the solids which are ordinarily poor conductors of electricity below their m.p. suddenly become good conductors. This is because during melting the ions become free to [illegible]

4. **Products of Electrolysis.**—[illegible] through an electrolyte (say hydrochloric acid, [illegible]) and Cl⁻ in this case) move towards oppositely charged electrodes, lose their charge and are liberated as hydrogen and chlorine. These changes can be represented as follows:



$HCl \rightleftharpoons H^+ + Cl^-$ [illegible]

$H^+ + e^- \rightarrow H$ [illegible]

From cathode

$H + H \rightarrow H_2$ (At cathode)

$Cl^- \rightarrow Cl + e^-$

Given to anode

$Cl + Cl \rightarrow Cl_2$ (At anode)

Usually there are several different kinds of ions around each electrode competing for electrons at the cathode and competing for an opportunity for giving up electrons at the anode. It [illegible] found experimentally that [illegible]

*See Ionic Theory—Chapter [illegible].

A metallic conductor behaves as if it contains electrons which are relatively free to move. An electric current flows through the metallic conductors as a result of the flow of electrons. The passage of current through such a conductor has no observable effect other than that of raising its temperature. An electrolyte in its fused state or its aqueous solution contains no detectable concentration of electrons. It conducts electricity not by virtue of the flow of electrons but as a result of the movement of ions which are electrically charged. When current traverses the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from an ion. Removal of electrons from atoms, molecules or ions is termed *oxidation (de-electronation)* while addition of electrons to atoms, radicals or ions is called *reduction (Electronation).* Hence flow of electrons across the boundary is accompanied by oxidation or reduction.

Conduction of current through a metallic conductor and an electrolytic conductor may be briefly distinguished as below:

Metallic conduction	Electrolytic conduction
1. It consists of the flow of electrons in the conductor.	1. It consists of the movement of ions in solution or a fused electrolyte.
2. It involves no change in the chemical properties of the conductor.	2. It involves chemical reactions which take place at electrodes (see electrolysis below).
3. It does not involve the transfer of any matter.	3. It involves transfer of matter in the form of ions.
4. It generally shows increase in resistance as temperature is increased.	4. It generally shows a decrease in resistance as the temperature is increased because the viscosity of the medium and the degree of hydration of the ions decreases with increasing temperature.

3. **Electrolysis.** *The process of decomposition of an electrolyte by passage of electric current through it is called* **electrolysis.** To bring about the electrolysis of a solution, we are required to dip two metallic rods or plates in the solution and connect them by means of a wire to the two terminals of a battery. These metallic rods or plates which lead the electric current to and from the electrolyte are termed **Electrodes.** The electrode connected with the positive pole of the battery is called the positive electrode or the **Anode** while the other connected with the negative pole of the battery is called the negative electrode or the **Cathode.** The current enters the electrolyte through the anode and leaves through the cathode.

Molecules of an electrolyte when dissolved in water split up into negatively and positively charged particles called **Ions** while

the process of splitting up of the molecules is called Ionization.* On electrolysis, positively charged ions move towards the cathode and are called Cations. The negatively charged ions which move towards the anode are called Anions.

At the cathode positively charged ions (cations) receive electrons and are thereby reduced. At the anode negatively charged ions (anions) lose electrons and are, therefore, oxidized.

The study of solutions of electrolytes and of the phenomena occurring at electrodes immersed in these solutions is termed Electro-chemistry. It is interesting to note that physical chemistry emerged as a distinct science in the field of electrochemistry.

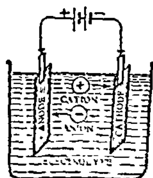
3. **Conductance of Solutions.**—Conductance of an electrolyte is due to the presence of these ions.

It depends on:

(*i*) the number of ions per unit volume.

(*ii*) the charge on the ions, and

(*iii*) the speed with which the ions move.



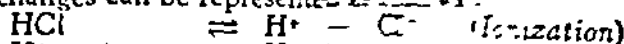
F g. [illegible]—Movement of the ions towards oppositely charged electrodes during electrolysis

(*a*) **On dilution**, the total number of ions in a weak electrolyte increases but the number of ions per unit volume decreases. As a result of it, the conductance decreases.

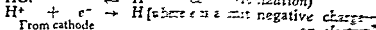
(b) **On heating**, the viscosity of the solution is lowered and thus the speed of the ions increases. Consequently the conductance of the solution increases.

(*c*) **On melting**, the solids which are ordinarily poor conductors of electricity below their m.p. suddenly become good conductors. This is because during melting the ions become free to move.

4. **Products of Electrolysis.**—On passing electric current through an electrolyte (say hydrochloric acid HCl), the ions (H^+ and Cl^- in this case) move towards oppositely charged electrodes, lose their charge and are liberated as hydrogen and chlorine gas. These changes can be represented as follows:



$$HCl \rightleftharpoons H^+ + Cl^- \quad \text{(Ionization)}$$



$$\underset{\text{From cathode}}{H^+ + e^-} \rightarrow H$$ [where *e* is a unit negative charge—an electron]



$$H + H \rightarrow H_2 \quad \text{(At cathode)}$$



$$Cl^- \rightarrow Cl + \underset{\text{Given to anode}}{e^-}$$



$$Cl + Cl \rightarrow Cl_2 \quad \text{(At anode)}$$

Usually there are several different kinds of ions [illegible] electrode competing for electrons at the cathode and [illegible] for an opportunity for giving up electrons at the [illegible] found experimentally that if a mixture of ions is [illegible]

*See Ionic Theory—Chapter 22.

A metallic conductor behaves as if it contains electrons which are relatively free to move. An electric current flows through the metallic conductors as a result of the flow of electrons. The passage of current through such a conductor has no observable effect other than that of raising its temperature. An electrolyte in its fused state or its aqueous solution contains no detectable concentration of electrons. It conducts electricity not by virtue of the flow of electrons but as a result of the movement of ions which are electrically charged. When current traverses the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from an ion. Removal of electrons from atoms, molecules or ions is termed *oxidation (de-electronation)* while addition of electrons to atoms, radicals or ions is called *reduction (Electronation)*. ence flow of electrons across the boundary is accompanied by oxidation or reduction.

Conduction of current through a metallic conductor and an electrolytic conductor may be briefly distinguished as below:

Metallic conduction	*Electrolytic conduction*
1. It consists of the flow of electrons in the conductor.	1. It consists of the movement of ions in solution or a fused electrolyte.
2. It involves no change in the chemical properties of the conductor.	2. It involves chemical reactions which take place at electrodes (see electrolysis below).
3. It does not involve the transfer of any matter.	3. It involves transfer of matter in the form of ions.
4. It generally shows increase in resistance as temperature is increased.	4. It generally shows a decrease in resistance as the temperature is increased because the viscosity of the medium and the degree of hydration of the ions decreases with increasing temperature.

2. **Electrolysis.**—*The process of decomposition of an electrolyte by passage of electric current through it is called* electrolysis. To bring about the electrolysis of a solution, we are required to dip two metallic rods or plates in the solution and connect them by means of a wire to the two terminals of a battery. These metallic rods or plates which lead the electric current to and from the electrolyte are termed **Electrodes**. The electrode connected with the positive pole of the battery is called the *positive electrode* or the **Anode** while the other connected with the negative pole of the battery is called the *negative electrode* or the **Cathode**. The current enters the electrolyte through the anode and leaves through the cathode.

Molecules of an electrolyte when dissolved in water split up into negatively and positively charged particles called **Ions** while

the process of splitting up of the molecules is called Ionization.* On electrolysis, positively charged ions move towards the cathode and are called Cations. The negatively charged ions which move towards the anode are called Anions.

At the cathode positively charged ions (cations) receive electrons and are thereby reduced. At the anode negatively charged ions (anions) lose electrons and are, therefore, oxidized.

The study of solutions of electrolytes and of the phenomena occurring at electrodes immersed in these solutions is termed Electro-chemistry. It is interesting to note that physical chemistry emerged as a distinct science in the field of electrochemistry.

3. Conductance of Solutions.—Conductance of an electrolyte is due to the presence of these ions.

It depends on :

(i) the number of ions per unit volume.

(ii) the charge on the ions, and

(iii) the speed with which the ions move.

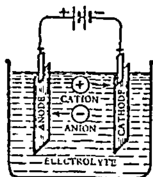


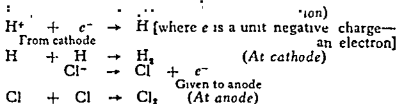
Fig. 21·2—Movement of the ions towards oppositely charged electrodes during electrolysis.

(a) On dilution, the total number of ions in a weak electrolyte increases but the number of ions per unit volume decreases. As a result of it, the conductance decreases.

(b) On heating, the viscosity of the solution is lowered and thus the speed of the ions increases. Consequently the conductance of the solution increases.

(c) On melting, the solids which are ordinarily poor conductors of electricity below their m.p. suddenly become good conductors. This is because during melting the ions become free to move.

4. Products of Electrolysis.—On passing electric current through an electrolyte (say hydrochloric acid, HCl), the ions (H^+ and Cl^- in this case) move towards oppositely charged electrodes, l[illegible] chlorine gas.
T[illegible]


[illegible] ion)

$H^+ + e^- \rightarrow H$ [where e is a unit negative charge—an electron]
(From cathode)

$H + H \rightarrow H_2$ (*At cathode*)

$Cl^- \rightarrow Cl + e^-$
(Given to anode)

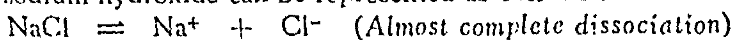
$Cl + Cl \rightarrow Cl_2$ (*At anode*)

Usually there are several different kinds of ions around each electrode competing for electrons at the cathode and competing for an opportunity for giving up electrons at the anode. It is found experimentally that if a mixture of ions is electrolysed,

*See Ionic Theory—Chapter 22.

certain ions are liberated at the electrodes in preference to others. This is explained by **Preferential Discharge Theory** which states that *if more than one type of ion is attracted to a given electrode, then the one liberated is the ion which requires least energy.* A measure of the energy required to liberate an ion is provided by the potential difference which must be applied between the electrodes to effect electrolysis. This potential is termed *discharge potential* or *deposition potential*.

For example, discharge potential of H^+ ions is lower than that of Na^+ ions when platinum or most of other metals are used as cathode. Similarly discharge potential of Cl^- ions is lower than that of OH^- ions. Hence electrolysis of an aqueous solution of sodium chloride (containing Na^+, H^+, Cl^- and OH^-) for manufacture of sodium hydroxide can be represented as follows :

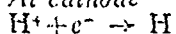


$$NaCl \rightleftharpoons Na^+ + Cl^- \quad \textit{(Almost complete dissociation)}$$

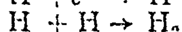


$$H_2O \rightleftharpoons H^+ + OH^- \quad \textit{(Very slight dissociation)}$$

At cathode



$$H^+ + e^- \rightarrow H$$

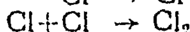


$$H + H \rightarrow H_2$$

At anode

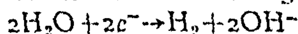


$$Cl^- \rightarrow Cl + e^-$$

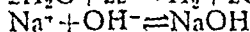


$$Cl + Cl \rightarrow Cl_2$$

Na^+ ions move to the cathode and combine with the OH^- ions formed due to reduction of water to give sodium hydroxide.



$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

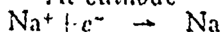


$$Na^+ + OH^- \rightleftharpoons NaOH$$

It is interesting to note that the H^+ ions which are present only in traces in a solution of sodium chloride get discharged in preference to Na^+ ions, at the cathode.

If, however, mercury is used as cathode as in Castner-Kellner cell, the Na^+ ions have lower discharge potential than H^+ ions. Hence Na^+ are discharged in preference to H^+. Na^+ ions lose their charge at the cathode and the atoms combine with mercury to form sodium amalgam which then reacts with water forming sodium hydroxide and hydrogen.

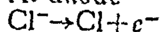
At cathode



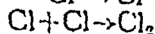
$$Na^+ + e^- \rightarrow Na$$

(Form amalgam)

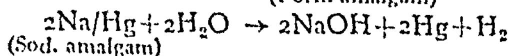
At anode



$$Cl^- \rightarrow Cl + e^-$$



$$Cl + Cl \rightarrow Cl_2$$

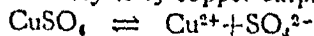


$$2Na/Hg + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

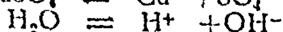
(Sod. amalgam)

A few more examples of electrolytic reactions are given below :

(*i*) *Electrolysis of copper sulphate using platinum electrodes.*

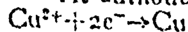


$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-} \quad \textit{(Ionization)}$$



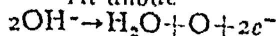
$$H_2O \rightleftharpoons H^+ + OH^- \quad \textit{(Slight dissociation)}$$

At cathode

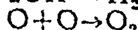


$$Cu^{2+} + 2e^- \rightarrow Cu$$

At anode



$$2OH^- \rightarrow H_2O + O + 2e^-$$

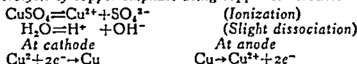


$$O + O \rightarrow O_2$$

Discharge potential of Cu^{2+} ions being lower than that of H^+ ions, these are discharged in preference to H^+. Hence copper atoms get deposited on the platinum cathode. In the anodic compartment OH^- ions have lower discharge potential as compared with the SO_4^{2-} ions. Hence OH^- ions (in spite of their lower

concentration) are discharged in preference to SO_4^{2-} ions and yield water and oxygen as shown above.

(ii) *Electrolysis of copper sulphate using copper electrodes.*



$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$ (*Ionization*)

$H_2O \rightleftharpoons H^+ + OH^-$ (*Slight dissociation*)

At cathode — $Cu^{2+} + 2e^- \rightarrow Cu$

At anode — $Cu \rightarrow Cu^{2+} + 2e^-$

Here also the discharge potential of Cu^{2+} ions being lower than that of H^+ ions these are discharged in preference to H^+ ions. Thus copper is deposited on the cathode.

Three possible anodic processes are :

(*a*) Solution of copper to form Cu^{2+} ions.



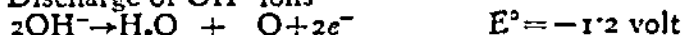
$Cu \rightarrow Cu^{2+} + 2e^-$ $E^\circ = -0·34$ volt

(*b*) Discharge of SO_4^{2-} ions



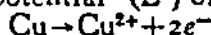
$SO_4^{2-} \rightarrow SO_4 + 2e^-$ $E^\circ = -2·0$ volts

(*c*) Discharge of OH^- ions



$2OH^- \rightarrow H_2O + O + 2e^-$ $E^\circ = -1·2$ volt

Oxidation potential* (E°) of



$Cu \rightarrow Cu^{2+} + 2e^-$

being the lowest, copper anode dissolves in preference to the other processes.

5. **Faraday's Laws of Electrolysis.**—During his studies on electrolysis, Michael Faraday deduced the following laws first stated in 1834.

First Law : *The weight of an ion liberated during electrolysis is proportional to the quantity of electricity passed.* Or mathematically :

$$W \propto Q$$
$$\propto Ct$$

or
$$W = CtZ$$

where

W=Wt. of the ions liberated ;

Q=Quantity of electricity in coulombs ;

C=Strength of current in amperes ;

t=Time in seconds ; while Z is a constant of proportionality and is called the electro-chemical equivalent.



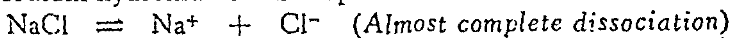
Michael Faraday
(1791—1867)
An English physicist and chemist, is well known for the outstanding work on electrolysis.

*The formation of a metal ion in aqueous solution can be formulated as the sum of the following stepwise changes :

Step :		*Energy change*
(i) $M_{(s)}$	$\rightarrow M_{(g)}$	Sublimation energy
(ii) $M_{(g)}$	$\rightarrow M^{n+}_{(g)} + ne^-$	Ionization potential
(iii) $M^{n+}_{(g)}$	$\rightarrow M^{n+}_{(aq)}$	Energy of solvation of ion
$M_{(s)}$	$\rightarrow M^{n+}_{(aq)}$	Energy of overall electrode process termed electrode potential or oxidation potential.

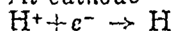
certain ions are liberated at the electrodes in preference to others. This is explained by **Preferential Discharge Theory** which states that *if more than one type of ion is attracted to a given electrode, then the one liberated is the ion which requires least energy.* A measure of the energy required to liberate an ion is provided by the potential difference which must be applied between the electrodes to effect electrolysis. This potential is termed *discharge potential* or *deposition potential*.

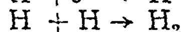
For example, discharge potential of H^+ ions is lower than that of Na^+ ions when platinum or most of other metals are used as cathode. Similarly discharge potential of Cl^- ions is lower than that of OH^- ions. Hence electrolysis of an aqueous solution of sodium chloride (containing Na^+, H^+, Cl^- and OH^-) for manufacture of sodium hydroxide can be represented as follows :


$NaCl \rightleftharpoons Na^+ + Cl^-$ *(Almost complete dissociation)*

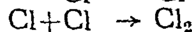

$H_2O \rightleftharpoons H^+ + OH^-$ *(Very slight dissociation)*

At cathode | *At anode*

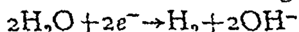

$H^+ + e^- \rightarrow H$

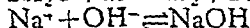

$H + H \rightarrow H_2$


$Cl^- \rightarrow Cl + e^-$


$Cl + Cl \rightarrow Cl_2$

Na^+ ions move to the cathode and combine with the OH^- ions formed due to reduction of water to give sodium hydroxide.


$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$


$Na^+ + OH^- \rightleftharpoons NaOH$

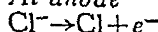
It is interesting to note that the H^+ ions which are present only in traces in a solution of sodium chloride get discharged in preference to Na^+ ions, at the cathode.

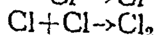
If, however, mercury is used as cathode as in Castner-Kellner cell, the Na^+ ions have lower discharge potential than H^+ ions. Hence Na^+ are discharged in preference to H^+. Na^+ ions lose their charge at the cathode and the atoms combine with mercury to form sodium amalgam which then reacts with water forming sodium hydroxide and hydrogen.

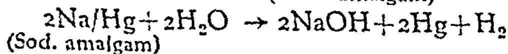
At cathode | *At anode*


$Na^+ + e^- \rightarrow Na$

(Form amalgam)


$Cl^- \rightarrow Cl + e^-$


$Cl + Cl \rightarrow Cl_2$

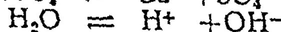

$2Na/Hg + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$

(Sod. amalgam)

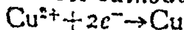
A few more examples of electrolytic reactions are given below :

(i) *Electrolysis of copper sulphate using platinum electrodes.*

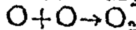

$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$ *(Ionization)*


$H_2O \rightleftharpoons H^+ + OH^-$ *(Slight dissociation)*

At cathode | *At anode*


$Cu^{2+} + 2e^- \rightarrow Cu$

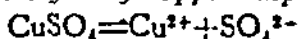

$2OH^- \rightarrow H_2O + O + 2e^-$


$O + O \rightarrow O_2$

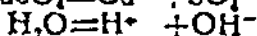
Discharge potential of Cu^{2+} ions being lower than that of H^+ ions, these are discharged in preference to H^+. Hence copper atoms get deposited on the platinum cathode. In the anodic compartment OH^- ions have lower discharge potential as compared with the SO_4^{2-} ions. Hence OH^- ions (in spite of their lower

concentration) are discharged in preference to SO_4^{2-} ions and yield water and oxygen as shown above.

(ii) *Electrolysis of copper sulphate using copper electrodes.*

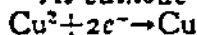


$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$ (*Ionization*)

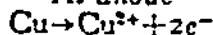


$H_2O \rightleftharpoons H^+ + OH^-$ (*Slight dissociation*)

At cathode *At anode*



$Cu^{2+} + 2e^- \rightarrow Cu$



$Cu \rightarrow Cu^{2+} + 2e^-$

Here also the discharge potential of Cu^{2+} ions being lower than that of H^+ ions these are discharged in preference to H^+ ions. Thus copper is deposited on the cathode.

Three possible anodic processes are :

(*a*) Solution of copper to form Cu^{2+} ions.



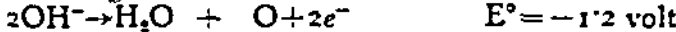
$Cu \rightarrow Cu^{2+} + 2e^-$ $E^\circ = -0{\cdot}34$ volt

(*b*) Discharge of SO_4^{2-} ions



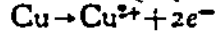
$SO_4^{2-} \rightarrow SO_4 + 2e^-$ $E^\circ = -2{\cdot}0$ volts

(*c*) Discharge of OH^- ions



$2OH^- \rightarrow H_2O + O + 2e^-$ $E^\circ = -1{\cdot}2$ volt

Oxidation potential* (E°) of



$Cu \rightarrow Cu^{2+} + 2e^-$

being the lowest, copper anode dissolves in preference to the other processes.

5. **Faraday's Laws of Electrolysis.**—During his studies on electrolysis, Michael Faraday deduced the following laws first stated in 1834.

First Law : *The weight of an ion liberated during electrolysis is proportional to the quantity of electricity passed.* Or mathematically :

$$W \propto Q$$
$$\propto Ct$$

or $$W = CtZ$$

where

W = Wt. of the ions liberated ;

Q = Quantity of electricity in coulombs ;

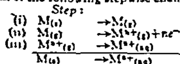
C = Strength of current in amperes ;

t = Time in seconds ; while Z is a constant of proportionality and is called the electro-chemical equivalent.



Michael Faraday (1791—1867)
An English physicist and chemist, is well known for the outstanding work on electrolysis.

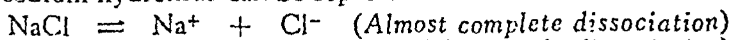
*The formation of a metal ion in aqueous solution can be formulated as the sum of the following stepwise changes :

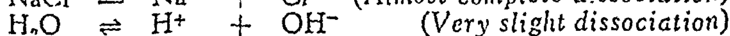


Step :		*Energy change*
(i) $M_{(s)}$	$\rightarrow M_{(g)}$	Sublimation energy
(ii) $M_{(g)}$	$\rightarrow M^{n+}_{(g)} + ne^-$	Ionization potential
(iii) $M^{n+}_{(g)}$	$\rightarrow M^{n+}_{(aq)}$	Energy of solvation of ion
$M_{(s)}$	$\rightarrow M^{n+}_{(aq)}$	Energy of overall electrode process termed electrode potential or oxidation potential.

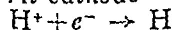
certain ions are liberated at the electrodes in preference to others. This is explained by **Preferential Discharge Theory** which states that *if more than one type of ion is attracted to a given electrode, then the one liberated is the ion which requires least energy.* A measure of the energy required to liberate an ion is provided by the potential difference which must be applied between the electrodes to effect electrolysis. This potential is termed *discharge potential or deposition potential.*

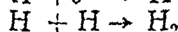
For example, discharge potential of H^+ ions is lower than that of Na^+ ions when platinum or most of other metals are used as cathode. Similarly discharge potential of Cl^- ions is lower than that of OH^- ions. Hence electrolysis of an aqueous solution of sodium chloride (containing Na^+, H^+, Cl^- and OH^-) for manufacture of sodium hydroxide can be represented as follows :


$NaCl \rightleftharpoons Na^+ + Cl^-$ (*Almost complete dissociation*)

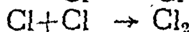

$H_2O \rightleftharpoons H^+ + OH^-$ (*Very slight dissociation*)

At cathode   *At anode*

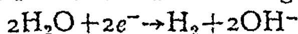

$H^+ + e^- \rightarrow H$

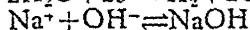

$H + H \rightarrow H_2$


$Cl^- \rightarrow Cl + e^-$


$Cl + Cl \rightarrow Cl_2$

Na^+ ions move to the cathode and combine with the OH^- ions formed due to reduction of water to give sodium hydroxide.

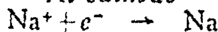

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$


$$Na^+ + OH^- \rightleftharpoons NaOH$$

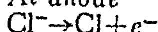
It is interesting to note that the H^+ ions which are present only in traces in a solution of sodium chloride get discharged in preference to Na^+ ions, at the cathode.

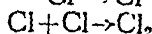
If, however, mercury is used as cathode as in Castner-Kellner cell, the Na^+ ions have lower discharge potential than H^+ ions. Hence Na^+ are discharged in preference to H^+. Na^+ ions lose their charge at the cathode and the atoms combine with mercury to form sodium amalgam which then reacts with water forming sodium hydroxide and hydrogen.

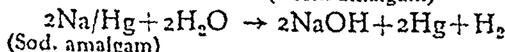
At cathode   *At anode*


$Na^+ + e^- \rightarrow Na$

(Form amalgam)


$Cl^- \rightarrow Cl + e^-$


$Cl + Cl \rightarrow Cl_2$

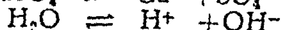

$2Na/Hg + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$

(Sod. amalgam)

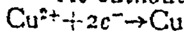
A few more examples of electrolytic reactions are given below :

(*i*) *Electrolysis of copper sulphate using platinum electrodes.*

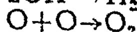

$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$ (*Ionization*)


$H_2O \rightleftharpoons H^+ + OH^-$ (*Slight dissociation*)

At cathode   *At anode*


$Cu^{2+} + 2e^- \rightarrow Cu$


$2OH^- \rightarrow H_2O + O + 2e^-$

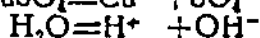

$O + O \rightarrow O_2$

Discharge potential of Cu^{2+} ions being lower than that of H^+ ions, these are discharged in preference to H^+. Hence copper atoms get deposited on the platinum cathode. In the anodic compartment OH^- ions have lower discharge potential as compared with the SO_4^{2-} ions. Hence OH^- ions (in spite of their lower

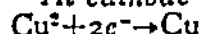
concentration) are discharged in preference to SO_4^{2-} ions and yield water and oxygen as shown above.

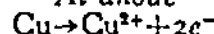
(ii) *Electrolysis of copper sulphate using copper electrodes.*


$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$ (*Ionization*)


$H_2O \rightleftharpoons H^+ + OH^-$ (*Slight dissociation*)

At cathode *At anode*

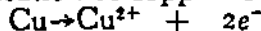

$Cu^{2+} + 2e^- \rightarrow Cu$


$Cu \rightarrow Cu^{2+} + 2e^-$

Here also the discharge potential of Cu^{2+} ions being lower than that of H^+ ions these are discharged in preference to H^+ ions. Thus copper is deposited on the cathode.

Three possible anodic processes are :

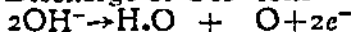
(*a*) Solution of copper to form Cu^{2+} ions.


$Cu \rightarrow Cu^{2+} + 2e^-$ $E^\circ = -0·34$ volt

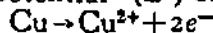
(*b*) Discharge of SO_4^{2-} ions


$SO_4^{2-} \rightarrow SO_4 + 2e^-$ $E^\circ = -2·0$ volts

(*c*) Discharge of OH^- ions


$2OH^- \rightarrow H_2O + O + 2e^-$ $E^\circ = -1·2$ volt

Oxidation potential* (E°) of


$Cu \rightarrow Cu^{2+} + 2e^-$

being the lowest, copper anode dissolves in preference to the other processes.

5. **Faraday's Laws of Electrolysis.**—During his studies on electrolysis, Michael Faraday deduced the following laws first stated in 1834.

First Law : *The weight of an ion liberated during electrolysis is proportional to the quantity of electricity passed.* Or mathematically :

$$W \propto Q$$
$$\propto Ct$$

or $$W = CtZ$$

where

W = Wt. of the ions liberated ;

Q = Quantity of electricity in coulombs ;

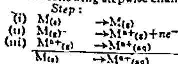
C = Strength of current in amperes ;

t = Time in seconds ; while Z is a constant of proportionality and is called the **electro-chemical equivalent.**



Michael Faraday
(1791—1867)
An English physicist and chemist, is well known for the outstanding work on electrolysis.

*The formation of a metal ion in aqueous solution can be formulated as the sum of the following stepwise changes :



Step :		*Energy change*
(i) $M_{(s)}$	$\rightarrow M_{(g)}$	Sublimation energy
(ii) $M_{(g)}$	$\rightarrow M^{n+}_{(g)} + ne^-$	Ionization potential
(iii) $M^{n+}_{(g)}$	$\rightarrow M^{n+}_{(aq)}$	Energy of solvation of ion
$M_{(s)}$	$\rightarrow M^{n+}_{(aq)}$	Energy of overall electrode process termed electrode potential or oxidation potential.

1·204 When $C = 1$ ampere and $t = 1$ second ;

$$W = Z$$

i.e., electro-chemical equivalent of an ion is the weight of the ion deposited by one ampere current in one second.

Second Law. *When the same quantity of electricity passes through different electrolytes, the weights of different ions liberated at the electrodes are in the ratio of their chemical equivalents.*

For example, if the same current be passed through a number of voltameters arranged in series as shown in the diagram (Fig. 21·3) then the weights of hydrogen, copper, silver and tin deposited on respective cathodes will be in the ratio of their chemical equivalents.

$$\frac{\text{Wt. of copper}}{\text{Wt. of silver}} = \frac{\text{Eq. wt. of copper}}{\text{Eq. wt. of silver}} \text{ and so on.}$$

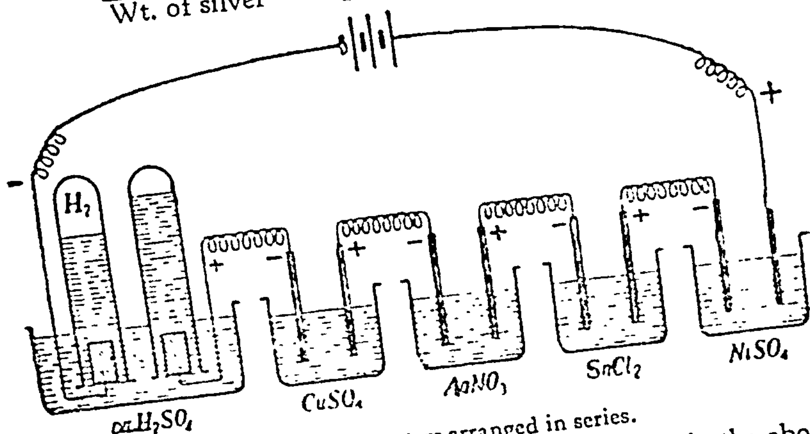


Fig. 21·3—Voltameters arranged in series.

If the passage of electric current is continued in the above voltameters until 1·008 gm. of hydrogen (one gm. equivalent weight) is evolved from the sulphuric acid solution, the weights of copper, silver and tin deposited will be found to be one gram equivalent weight in each case. It is found that 96,540 coulombs of electricity are required to liberate one gram-equivalent weight of any element. This much quantity of electricity is named one faraday. The fact can be employed to find the electro-chemical equivalents of different substances. For example,

$$\text{Electro-chemical equivalent of Silver} = \frac{\text{Gram eq. wt.}}{96{,}540}$$

$$= \frac{107·88}{96{,}540} = 0·001118 \text{ gm.}$$

$$\text{Electro-chemical equivalent of Copper} = \frac{31·78}{96{,}540} = 0·0003293$$

$$\text{Electro-chemical equivalent of Hydrogen} = \frac{1·008}{96{,}540} = 0·00001045$$

process (to count the number of coulombs passed and to weigh the products formed) and their accuracy is limited only by the accuracy of measuring the chemical changes and the quantity of electricity.

It is interesting to note that it was as a consequence of Faraday's Laws of electrolysis that the idea of the fundamental particle of electricity came into being. It was argued that, since 1 gram equivalent of any substance is associated with F coulombs of electricity, one gram ion must be associated with ZF coulombs, where Z is the valency. Therefore, one ion of any substance must be associated with ZF/N coulombs (one gram ion contains Avogadro number, $N=6{\cdot}023\times10^{23}$ ions) As Z is a whole number, this quantity is a simple multiple of the quantity F/N. Thus F/N is the smallest quantity of electricity ever found associated with an atom in the form of an ion.
in nature, and F/N is the 'at
fundamental unit of electrici
suggestion of G. Johnstone Stoney (1891). Accurate estimate of Avogadro number N is obtained by dividing the faraday by the charge of an electron.

$$N=\frac{F}{e}=\frac{96{,}540}{1{\cdot}601\times10^{-19}}=6{\cdot}023\times10^{23}$$

$\therefore$ Electronic charge $=4{\cdot}803\times10^{-10}$ *esu*

$=1{\cdot}601\times10^{-19}$ coulombs

Example 1. *A current of 0·5 ampere is passed for 30 minutes through a voltameter containing copper sulphate solution. What is the weight of copper deposited? (At. wt. of copper=63·6).*

Here $C=0{\cdot}5$ ampere.

$t=30\times60=1800$ seconds.

$Q=Ct=0{\cdot}5\times1800=900$ coulombs.

From the reaction at the cathode



$$Cu^{2+} + 2e^- \rightarrow Cu$$

the number of electrons involved per atom of copper being 2.

$$\text{Eq. wt. of copper}=\frac{\text{At. wt.}}{2}=\frac{63{\cdot}6}{2}=31{\cdot}8$$

Now 96,540 coulombs (1 faraday) of electricity will deposit one gm. eq. wt =(31·8 gm.) of copper.

$$\text{Wt. of copper liberated by 900 coulombs}=\frac{31{\cdot}8}{96{,}540}\times900$$

$$=0{\cdot}2964 \text{ gm.}$$

Example 2. *A current was passed in series through a solution of a salt of a metal X and a solution of $ZnSO_4$, platinum electrodes being used. After a certain time, 0·348 gm. of X and 1·264 gm. of Zn had been deposited. Calculate the eq. wt. of X. Equivalent weight of zinc is 32·7.*

$$\frac{\text{Eq. wt. of X}}{\text{Eq. wt. of Zn}}=\frac{\text{Wt. of X}}{\text{Wt. of Zn}}$$ (Both deposited by the same quantity of current)

$$\therefore \quad \frac{\text{Eq. wt. of X}}{32{\cdot}7}=\frac{0{\cdot}348}{1{\cdot}264}$$

or $$\text{Eq. wt. of X}=\frac{0{\cdot}348}{1{\cdot}264}\times 32{\cdot}7=9{\cdot}0.$$

6. **Applications of Electrolysis.**—A few of the important applications of the phenomenon of electrolysis are given below :

(1) **Electroplating.**

What is it ? The art of depositing a superior metal over another baser metal with the help of electric current is called *Electroplating*. The object in carrying out the process is *either*—

(i) *Preservation*, e.g., iron is electroplated with tin or chromium to prevent rusting, or

(ii) *Decoration*, e.g., a copper tea-set is silver plated to enhance its beauty.

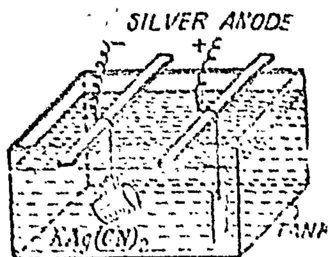


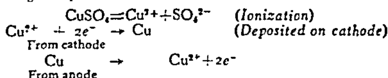
Fig. 21·4 -Silverplating of a tea-cup.

Process. The article to be electroplated is cleaned thoroughly—mechanically or chemically—and made the cathode in an electrolytic bath where the anode is made of the metal which is to form the outer coating, e.g., silver anode is used in silver plating. The **electrolyte** is any soluble salt of the metal. Suitable electrolyte should be (i) highly soluble, (ii) good conductor, (iii) stable towards oxidation, reduction or hydrolysis, and (iv) cheap. Generally mixtures are used to satisfy all the requisites. For example, acidified copper sulphate solution is used in copper plating ; nickel ammonium sulphate is used in nickel plating ; double cyanide of silver and potassium, $KAg(CN)_2$ is used in silver plating while double cyanide of gold and potassium is used in gold plating.

The vessel in which electrolyte is placed and electrodes are suspended is called a **Tank.** It is made of glass, enamelled iron, wood, stone or cement. The choice of the tank material depends upon the nature of the electrolyte and cost. On passing electric current, a thin coating of superior metal is obtained on the article made as the cathode.

Nature of deposit. The deposit is found to be crystalline and its quality depends on the size of crystals. Finer the crystals, smoother and brighter the deposit. *Low temperature, high current density and high metal concentration* are the conditions which favour the deposition of fine crystals or smooth and bright deposit.

Theory. Deposit of copper from copper sulphate bath in copper plating is explained as below :



$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-} \quad \textit{(Ionization)}$$

$$\underset{\text{From cathode}}{Cu^{2+} + 2e^-} \rightarrow Cu \quad \textit{(Deposited on cathode)}$$

$$\underset{\text{From anode}}{Cu} \rightarrow Cu^{2+} + 2e^-$$

As is clear from above Cu^{2+} ions move to the cathode, lose their charge and are deposited on the cathode. At anode oxidation potential being the lowest, copper anode ($E°$of $Cu \rightarrow Cu^{2+} + 2e^-$) *dissolves in preference to other processes. This continues, till* a thin coating of copper is obtained on the article to be electroplated.

Electroplating with gold, silver, nickel, chromium or rubber is carried out in a similar manner.

(2) **Electro-refining of Metals.** This is the modern method of refining impure metals. Copper, silver, zinc, aluminium, tin and lead are purified elecrolytically.

(The impute metal is made the anode in an electrolytic bath containing solution of a soluble salt of the metal. Thin sheets of pure metal are made the cathode. On passing electric current, pure metal from the electrolyte deposits on the cathode and an equivalent amount is dissolved from the anode. Impurities present either pass into solution or fall down as 'anode mud'?

(3) **Electrotyping** In large-scale printing impression of the ordinary type page is made in wax or plaster of Paris. The wax plate is made a conductor by sprinkling graphite on it and then made cathode in a copper-plating bath On passing electric current copper deposits on the wax plate till sufficient thickness of copper deposit is obtained. It is removed and strengthened by filling its back with type-metal The mould obtained is an exact copy of the printer's page and is used in large-scale printing

(4) **Electrometallurgy.** *The process of extraction of metal from its ore by electrolysis is called* **electrometallurgy.** For example, sodium is obtained by electrolysis of fused sodium hydroxide or sodium chloride while aluminium is extracted by electrolysis of bauxite in fused cryolite.

(5) **Industrial Preparations.** A large number of chemicals used in industry and medicine are prepared electrolytically. Fo

example, caustic soda, washing soda, chlorine are obtained by electrolysis of sodium chloride while hydrogen and oxygen are manufactured by electrolysis of acidulated water.

(6) **Determination of Equivalent Weights.** This is based on Faraday's Second Law of Electrolysis (*see* page 1·204).

QUESTIONS AND PROBLEMS

Essay-type Questions :

1. (*a*) Define electrode, electrolyte, electrolysis and a non-electrolyte. State Faraday's Law of Electrolysis. Give four applications of the phenomenon of electrolysis. (*Punjab Pre-Univ. 1971, 64*)

(*b*) Write a short note on Electroplating. (*Delhi H.S. 1970*)

(*c*) Write a detailed note on Faraday''s laws of electrolysis and their applications. (*Delhi H.S. 1972*)

2. (*a*) State and explain fully Faraday's Law of Electrolysis. What information do these laws provide on the nature of matter and electricity ?

(*b*) Find the weight of copper deposited from copper sulphate solution by a current of 0·25 ampere flowing for one hour. [*At. Wt. of Cu=63 ; faraday =96,540 coulombs*]. (*Punjab-Pre-Univ. 1970 ; Delhi H S. 1964, 61, 60 ; Delhi Prep. 1961, 60*)

(*c*) A current of 2 amperes was passed through a solution of copper sulphate for 16 minutes and 5 seconds. Calculate the amount of copper deposited. [*At. wt. of Cu=63·6 ; 1 faraday=96,500 coulombs*]. (*Delhi Pre-Medical 1964*)

3. (*a*) State Faraday's Laws of Electrolysis. How does the Second Law of Electrolysis help in the determination of the equivalent weight of a metal ? (*Delhi H.S. 1970 ; Kashmir Inter. 1961*)

(*b*) A current of 3 amp. strength passing through silver nitrate solution for 20 minutes deposited 4 gm. of silver. What is the electro-chemical equivalent of silver ? (*Delhi Prep. 1961*)

4. An electric current is passed through a solution of copper sulphate and cyanide of silver connected in series. If in a given time 0·35 gm. of copper is deposited, what will be the weight of silver deposited in the same time ? [*At. wt. of copper=63·57 ; Silver=107·88*]

5. Explain what happens when an electric current is passed through (*a*) sodium chloride solution between carbon electrodes, and (*b*) copper sulphate solution between copper electrodes.

Calculate in the case of (*a*) the amounts of products formed when the same current deposited 0·1118 gm. of silver in a voltameter in series. (*Punjab Inter. 1960*)

6. What is electrolysis ? Outline the observations of Faraday regarding this phenomenon. What happens when an electric current is passed through (*a*) solution of sodium chloride between carbon electrodes and (*b*) copper sulphate solution between copper electrodes.

A current of 0·1 ampere is passed for 45 minutes through a voltameter containing acidulated water and another containing copper sulphate solution with copper electrodes. What volume of oxygen gas at N.T.P. will be evolved in the first voltameter and what weight of copper deposited in the second ? (*Delhi Pre-Medical 1960*)

7. What is electrolysis ? State Faraday's Laws of Electrolysis. Explain clearly the formation of various products in the electrolysis of the following :

(*a*) Aqueous solution of copper sulphate between platinum electrodes, (*b*) Aqueous solution of silver nitrate between silver electrodes, (*c*) Fused calcium chloride between carbon electrodes, (*d*) Solution of sodium chloride, (*e*) Dilute sulphuric acid. (*Punjab H.S. 1963*)

8. Calculate the electro-chemical equivalent of silver and copper, given the electro-chemical equivalent of hydrogen=0·0000104; atomic weight of Ag=107·88 and atomic weight of Cu=63·54. *(I.I.T. Admission Test 1961)*

[Hint : Electro-chemical equivalent, $Z=\frac{\text{Gm. Eq. wt.}}{\text{faraday}}$

Here : Z for Ag=Z for H $\times\frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of H}}$].

9. On passing a [illegible] of a metal for 32 minu[illegible] is the equivalent weight [illegible]
(Bombay Inter. 1962)

10. An electric current is passed between platinum electrodes through solutions of silver nitrate, copper sulphate and dilute sulphuric acid, the solutions be[illegible] [illegible]y the current [illegible] second cell, [illegible] berated from [illegible] *(Bombay Inter. 1961)*

11. The molecular weights of hydrogen, chlorine and oxygen are 2, 71 and 32 respectively. The weights of these gases liberated in electrolysis by 96,500 coulombs of electricity are :

hydrogen=1 gm., chlorine=35·5 gm ; oxygen=8 gm.

Explain these figures.

Calculate the weight of metallic chromium deposited from a solution of chromic chloride ($CrCl_3$) by a current of 0·2 amp. passing for 100 minutes. *(Senior Cambridge 1966 July)*

12. An electric current is passed through two voltameters in series, one a copper voltmeter with copper electrodes in a solution of copper sulphate, the other with platinum electrodes in a dilute solution of sulphuric acid. After a time, 785 c.c. of hydrogen measured dry at 27°C and 745 mm are collected in one voltameter. What weight of copper will be deposited on the cathode in the other ? (Cu=64) *(Senior Cambridge 1966 Nov.)*

Test Your Understanding :

13. Fill in the blanks in the following :

(i) The process of decomposition of a/an. ....by passage of electric current through it is termed......

(ii) According to .. theory, if more than one type of ions are attracted towards a given electrode, then the one liberated is the ion which requires ......

(iii) ..... of an ion is the weight of the ion deposited by one ampere current in one second.

(iv) During electrolysis of brine ... ions are discharged as the cathode in a Nelson cell while ... ions are discharged as the cathode in a Castner-Kellner cell.

(v) Weight of an ion liberated during electrolysis is proportional to ...

Which of the following represents anodic process during electrolysis electrodes :

(a) $Cu \rightarrow Cu^{++} + 2e^-$; $E^\circ=-0·34$ volt

(b) $SO_4^{2-} \rightarrow SO_4 + 2e^-$; $E^\circ=-2·0$ volts

(c) $2OH^- \rightarrow H_2O + O+2e^-$; $E^\circ=-1·2$ volt

15. Dilute sulphuric acid is electrolysed using platinum electrodes. Which of the following things occur ?

	Cathode	*Anode*
(*a*)	Hydrogen is evolved.	Oxygen is evolved.
(*b*)	Oxygen is evolved.	the anode dissolves.
(*c*)	the cathode gains weight.	the anode dissolves.

KEY

13. (*i*) electrolyte, electrolysis ; (*ii*) Preferential discharge, least energy ; (*iii*) electrochemical equivalent ; (*iv*) H^+, Na^+ ; (*v*) the quantity of electricity passed.

14. (*a*). 15. (*a*).

ANSWERS

2. (*b*) 0·2936 gm. (*c*) 0·636 gm. 3. 0·00111. 4. 1·188

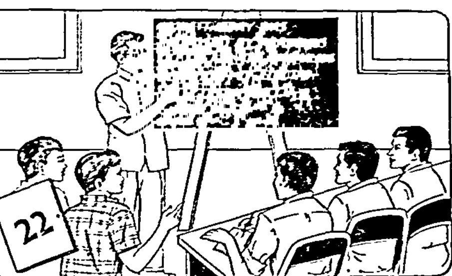
5. Hydrogen=0·001043 gm. ; Chlorine=0·03675 gm. Sodium hydroxide=0·04141 gm.

6. Oxygen=15·66 ml. ; Copper=0·08894 gm.

8. For Ag=0·001113 gm./coulomb ; For Cu=0·0003278 gm./coulomb.

9. 31·74. 10. Cu=0·2944 gm. H_2=103·7 c.c.

11. 0·216 gm. 12. 2·0 gm.



Ions in Solution

1. **Anomalous Behaviour of Electrolytes.**—Electrolytes lower the freezing point of a solvent more than non-electrolytes. For example, one gram mole of sugar when dissolved in 1000 grams of water, lowers its freezing point by 1·86°C. One gram molecule of sodium chloride or hydrochloric acid when dissolved in the same volume of water (1,000 grams) lowers the freezing point by nearly twice as much as sugar. Some electrolytes lower the freez- [illegible] others raise the boiling point nearly three times as much. Thus we see *that electrolytes affect the freezing and boiling points of a solvent abnormally.*

2. **The Theory of Ionization.**—To explain the anomalous behaviour of electrolytes, the Swedish chemist, Svante Arrhenius, proposed in 1887 his *theory of ionization*. In spite of the fact that it has undergone some changes since it was first proposed, his basic ideas are still accepted. According to him .

(a) By mere process of solution, the molecules of an electrolyte split up into negatively and positively charged particles called ions. *The process of splitting up of a molecule into ions is called* **ionization or dissociation.**

(b) The positively charged ions are called **cations** and the negatively charged ions are called **anions.**



Svant August Arrhenius
(1859—1925)
Swedish physicist and chemist; was awarded Nobel Prize for Chemistry in 1903 for his theory of electrolytic dissociation which he established in 1887.

(*c*) The aqueous solution of an electrolyte contains *an equal number of positive and negative charges.*

(*d*) In a solution only a fraction of the total number of molecules is ionized. This fraction is called **Degree of ionization** and depends upon the following factors :

(*i*) *The dilution*—it increases with dilution.

(*ii*) *The temperature*—it increases with temperature.

(*iii*) *The nature of solute.*

(*iv*) *The nature of solvent.* It is maximum in water.

(*v*) *The nature of other substances present in the solution.*

(*e*) Molecules of the solute are constantly splitting up into ions and the ions are constantly reuniting to give original molecules. There exists, thus, a state of **dynamic equilibrium** between unionized molecules on one side and ions on the other side. For example, in a sodium chloride solution, the equilibrium can be represented as



$$NaCl \rightleftharpoons Na^+ + Cl^-$$

(*f*) Conductivity of a solution is due to the concentration of ions present in the solution. The number of ions depends upon the degree of ionization. Greater the degree of ionization, larger the number of ions.

Conductivity is, therefore, proportional to the degree of ionization. The degree of ionization is, in fact, measured by measuring its electrical conductivity.

It is, however, interesting to note that although degree of ionization increases with dilution, the concentration of ions decreases due to the large increase in volume. Conductivity does not, therefore, increase with dilution.

Although the Arrhenius concept has been found definitely imperfect and inadequate, it has had a stimulating effect in promoting the progress of science. A large number of facts concerning electrolytes are beautifully explained in terms of theory of ionization and are given in the sections which follow. These facts furnish the evidence on which the theory is based.

3. **Evidence in favour of Ionic Theory.**—The Ionic Theory has been successful in explaining a number of phenomena like :—

(*i*) Strength of electrolytes.

(*ii*) Strength of acids and bases.

(*iii*) Ionic nature of reactions.

(*iv*) Neutralization.

(*v*) Electrolysis.

(*vi*) Hydrolysis.

(*vii*) Use of ammonium chloride in qualitative analysis and other related phenomena.

(*viii*) Abnormal behaviour of electrolytes in lowering the freezing point or raising the boiling point of a solvent to a greater extent than expected by adding definite quantities of these to fixed quantities of solvents.

These point towards the validity of the assumptions made by Arrhenius and thus constitute an evidence in favour of the ionic theory. The explanation of some of these phenomena in the light of ionic theory is given in the following sections.

4. Theory of Ionization and the Anomalous Behaviour of Electrolytes.—Lowering of freezing point and the elevation of boiling point of a solvent depend upon the number of particles of the solute. One gram molecular weight of every solute (electrolyte or non-electrolyte) contains the same number (Avogadro's number) of molecules. On dissolving 1 gm. mol. wt. of a non electrolyte in 100 gm. of water, the number of molecules in solution being fixed, produce the same depression in freezing point or elevation in boiling point.

On dissolving one gm. mol. wt. of an electrolyte in 100 gm. of water, ionization occurs. Some of the molecules split up into ions and the total number of particles (undissociated molecules+ions) increases. As the total number of particles increases, the depression in freezing point and the elevation of boiling point increase in the same proportion.

Thus anomalous behaviour of the electrolyes can be explained in the light of the theory of ionization.

5. Difference between an Atom and an Ion.—The points of difference between an atom and an ion can be summarized as follows :

(1) An atom is a neutral particle while an ion is a simple atom or a group of atoms carrying an electrical charge.

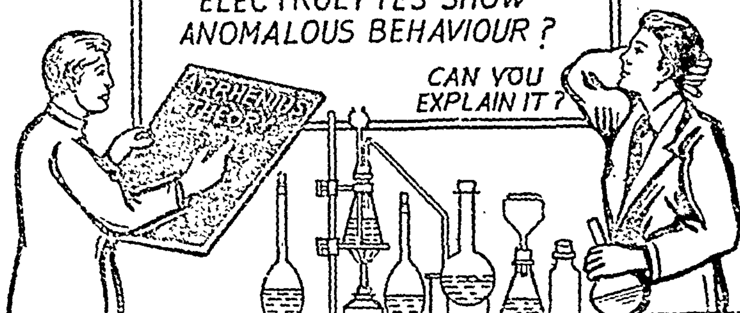
(2) An ion leads an independent existence in solution while an atom may or may not be capable of independent existence. For example, a sodium atom will at once react with water to produce sodium hydroxide and hydrogen while a sodium ion does not react with water at all.

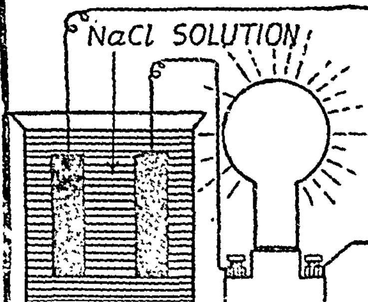
(3) Properties of an ion are entirely different from those of the atom. For example, sodium chloride gives a white precipitate of silver chloride with silver nitrate, due to the presence of chloride ions, Cl^- in sodium chloride solution Chloroform, $CHCl_3$, does not give any precipitate with silver nitrate due to the absence of chloride ions.

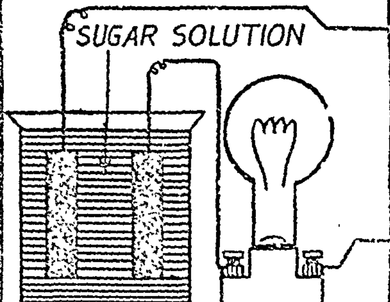
In other words, *an ion takes part in ionic reactions while an atom does not.*

On the other hand, *an atom takes part in a molecular reaction while an ion does not, e.g.*, sodium ion does not react as given under (2) above.

IONS IN SOLUTION









6. **Ionization *vs.* Dissociation.**—In the case of an electrolyte, ions already exist in the solid crystalline form. There they are

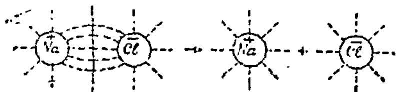
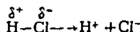


Fig 22 1—Dissociation of sodium chloride into ions.

held together by electrostatic lines of force. On dissolution, water (a solvent with high dielectric constant) merely decreases the attraction [illegible] movement in solution. [illegible] an independent existe[illegible] We say sodium chloride dissociates into sodium and chloride ions when it is dissolved in water.

Heating will produce the same effect. On melting, the ions present become mobile and the fused mass can conduct electricity.

Hydrogen chloride in the liquid state does not conduct electricity and is, therefore, a non-electrolyte. It is a covalent compound and the hydrogen and chlorine atoms are connected by a covalent bond. In H . Cl molecule, however, the shared pair of electrons is more towards chlorine (it being strongly electronegative). This gives Cl atom slightly negative charge and H-atom slightly positive charge. $\overset{\delta+}{H}-\overset{\delta-}{Cl}$ molecule is termed a polar molecule. On dissociation in water, the hydrogen chloride molecules are broken apart. The chlorine nucleus, being more strongly electropositive, retains both the shared electrons and becomes a chloride ion leaving behind hydrogen nucleus as hydrogen ion.



$$\overset{\delta+}{H}-\overset{\delta-}{Cl} \longrightarrow H^+ + Cl^-$$

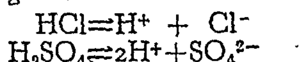
Here splitting of polar hydrogen chloride molecule, which does not contain any ions already, into hydrogen ions and chloride ions is called **Ionization**. *Thus electrovalent compounds dissociate whereas some covalent compounds ionize.*

[illegible]

another which produces few ions is termed a *weak electrolyte*.

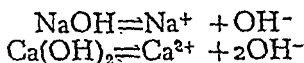
8. **Strength of Acids and Bases.**—An acid is a substance which can furnish hydrogen ions on ionization. Characteristic properties of an acid—sour taste, turns blue litmus red, neutralizes alkalis—are in fact properties of the hydrogen ions. *Strength*

an acid depends upon its degree of ionization—greater the degree of ionization, stronger the acid.



$$HCl \rightleftharpoons H^+ + Cl^-$$
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

An alkali or base is a substance which can furnish hydroxide ions on ionization. Characteristic properties of an alkali – bitter taste, turns red litmus blue and turmeric paper brown—are the properties characteristic of hydrogen ions. *Strength of a base depends upon its degree of ionization—greater the degree of ionization, stronger the base.*



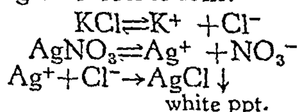
$$NaOH \rightleftharpoons Na^+ + OH^-$$
$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

Thus we see that the strength of an acid depends upon the concentration of hydrogen ions, $[H^+]$ present in the solution. In many acids this concentration is very low—of the order of 10^{-6} or thereabouts. So a convenient scale of expressing it, known as the *p*H scale, is used. A few illustrative examples are :

$[H^+]$ Concentration of hydrogen ion in solution	*pH of the solution*
1×10^{-1}	1
1×10^{-2}	2
1×10^{-3}	3
1×10^{-5}	5

It is clear that higher values of *p*H represent lower concen- ion of hydrogen ions. If *p*H is 7, the solution is neutral, le if *p*H is above 7 it is basic. In the same way, concentration)H⁻ in a solution is expressed as *p*OH. *The sum of pH and H in any aqueous solution is always 14.*

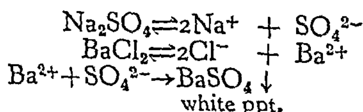
9. **Ionic Nature of Reactions.**—Most of the reactions in rganic analysis are in fact reactions of different ions. For mple, a chloride gives a white precipitate with silver nitrate spective of the nature of the metal radical (Na, K, Ca or Ba). s is because formation of a white precipitate with silver nitrate property of the chloride ions and silver ions. Ethyl chloride organic substance) does not give any white precipitate as it s not ionize to give chloride ions.



$$KCl \rightleftharpoons K^+ + Cl^-$$
$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$
$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

white ppt.

Similarly formation of white precipitate when barium chloride barium nitrate is added to sodium sulphate, potassium sulphate ammonium sulphate, is a property of sulphate ions and barium s

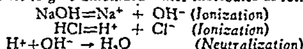


$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$
$$BaCl_2 \rightleftharpoons 2Cl^- + Ba^{2+}$$
$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$$

white ppt.

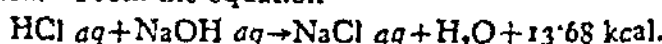
10. **Neutralization.**—It is the reaction of an acid with a base to produce a salt and water. According to the ionic theory, neutralization *is the process of combination of hydrogen ions from the*

ions further react to give unionized water molecules as follows :



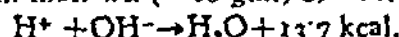
$$NaOH \rightleftharpoons Na^+ + OH^- \quad (Ionization)$$
$$HCl \rightleftharpoons H^+ + Cl^- \quad (Ionization)$$
$$H^+ + OH^- \rightarrow H_2O \quad (Neutralization)$$

11. **Heat of Neutralization.**—*The heat of neutralization is the number of calories liberated when a gram equivalent of an acid completely neutralizes a gram equivalent of a base in a dilute solution.* From the equation



$$HCl\ aq + NaOH\ aq \rightarrow NaCl\ aq + H_2O + 13{\cdot}68\ kcal.$$

13·68 kcal. of heat are evolved when a gm. eqvt of NaOH(= 40 gm.) neutralizes a gm. eqvt. of HCl (= 36·5 gm.) in dilute solution. The heat of neutralization of
mately constant (13·7 kcal
is not accompanied by an
of neutralization is the number of calories liberated during the formation of a gm. mol. wt. (= 18 gm.) of water from its ions.

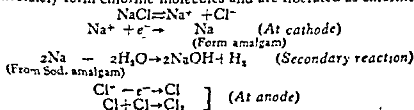


$$H^+ + OH^- \rightarrow H_2O + 13{\cdot}7\ kcal.$$

In the case of weak acids or bases some heat is absorbed or evolved during their ionization and as a result of it the heat of neutralization is either less or more than 13·7 kcal.

12. **Electrolysis.**—During electrolysis, the function of the electric current is to direct the ions, already present in the solution, towards oppositely charged electrodes where they lose their charge and are liberated as atoms or radicals. The atoms or radicals so obtained may remain as such or give rise to secondary reactions.

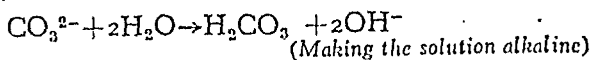
For example, during electrolysis of sodium chloride in a Casther-Kellner cell, sodium and chloride ions are already present in the solution. Sodium ions are directed by the electric current towards the cathode where they take one electron each and lose the positive charge. Sodium atoms so liberated form sodium amalgam with mercury. The amalgam reacts with water to give sodium hydroxide and hydrogen. The chloride ions, on the other hand, are directed towards the anode where they lose one electron (unit negative charge) each and are liberated as chlorine atoms which immediately form chlorine molecules and are liberated as chlorine.



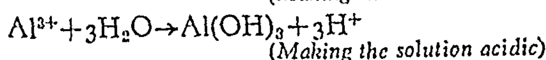
$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$Na^+ + e^- \rightarrow Na \quad (At\ cathode)$$
(Form amalgam)
$$2Na + 2H_2O \rightarrow 2NaOH + H_2 \quad (Secondary\ reaction)$$
(From Sod. amalgam)
$$\left.\begin{array}{l} Cl^- - e^- \rightarrow Cl \\ Cl + Cl \rightarrow Cl_2 \end{array}\right] \quad (At\ anode)$$

13. **Hydrolysis.**—Whenever the salt of either a weak acid or a weak base is dissolved in water, it reacts with water to give the original acid and base. The process which may be considered as reverse of neutralization is called **hydrolysis.**

Hydrolysis may also be defined as the reaction of the anions of weak acids (F^-, CO_3^{2-}, etc.) with water to form OH^- ions and the reaction of certain cations (*e.g.*, NH_4^+, Al^{3+}, Zn^{2+}) with water to form H^+ ions.

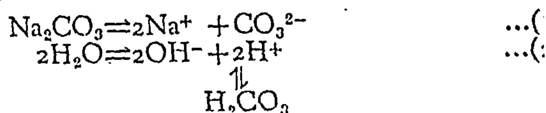


$$CO_3^{2-}+2H_2O \rightarrow H_2CO_3 +2OH^-$$
(*Making the solution alkaline*)



$$Al^{3+}+3H_2O \rightarrow Al(OH)_3+3H^+$$
(*Making the solution acidic*)

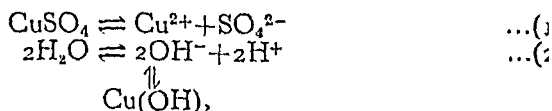
In terms of ionic theory, hydrolysis of sodium carbonate ca be explained as follows :



$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-} \quad ...($$
$$2H_2O \rightleftharpoons 2OH^- + 2H^+ \quad ...($$
$$\updownarrow$$
$$H_2CO_3$$

In a solution of sodium carbonate both water and sodiu carbonate ionize as given in (1) and (2) above. CO_3^{2-} from sodiu carbonate combine with H^+ from water to give nearly undissociate carbonic acid, H_2CO_3. Removal of H^+ shifts the equilibrium (to the right. Thus there is an accumulation of OH^- in a solutic which behaves alkaline towards litmus.

Similarly acidic nature of copper sulphate solution due to hy drolysis of copper sulphate can be explained as due to accumulatio of H^+ as a result of removal of OH^- by Cu^{2+} to form unionize $Cu(OH)_2$ as follows :



$$CuSO_4 \rightleftharpoons Cu^{2+}+SO_4^{2-} \quad ...($$
$$2H_2O \rightleftharpoons 2OH^-+2H^+ \quad ...($$
$$\updownarrow$$
$$Cu(OH)_2$$

A solution of sodium chloride or potassium chloride is neutr towards litmus. These are salts of strong acid (HCl) and stron bases (NaOH and KOH) and hence do not undergo hydrolysi Thus there is accumulation of neither H^+ ions nor OH^- ions an the solution is neutral.

14. **Solubility Product.**—*The ionic product in a saturate solution of an electrolyte is called its solubility product.* Ever electrolyte has a definite value of solubility product at a give temperature. Whenever the ionic product exceeds the solubilit product, some of the electrolyte is precipitated and the ioni product is again equal to the solubility product.

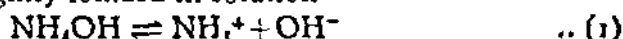
Some important applications of the principle of solubilit product in chemistry are given below :

(1) **Purification of Common salt.** In a saturated solutio of common salt, the ionic product is equal to the solubility product

On passing hydrogen chloride gas, the concentration of chloride ions increases in the solution and the ionic product of sodium chloride exceeds the solubility product. This results in precipitation of some pure sodium chloride. By continuing the passage of gas more and more of the salt is precipitated.

(2) **Salting out of soap.** Soap is the sodium salt of a higher fatty acid, say sodium stearate. On addition of sodium chloride *to a concentrated solution of soap, the concentration of sodium* ions increases in solution and the ionic product of sodium stearate exceeds the solubility product. This results in the precipitation of soap. *This process of precipitation of soap by adding common salt is called salting out of soap.*

(3) **Suppression of Ionization.** Ammonium hydroxide is a weak base and is slightly ionized in solution



$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad ..(1)$$

By adding ammonium chloride to the solution, we increase the concentration of ammonium ions $(NH_4)^+$ in the solution



$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \quad ...(2)$$

This shifts the equilibrium (1) above to the left, *ionization of ammonium hydroxide is suppressed by the common ion effect.*

The above idea of solubility product and Common Ion Effect finds numerous applications and some of those used in Analytical Chemistry are given below.

(*a*) **Use of Ammonium Chloride.** Ammonium chloride is used to produce a Common Ion Effect and suppress the ionization of *weak electrolytes* NH_4OH and $(NH_4)_2CO_3$ in the third and fifth groups of qualitative analysis respectively.

(*i*) **Precipitation of Hydroxide in Group III.** Ammonium hydroxide is a weak base and ionizes as given above. The concentration of OH^- ions though small is sufficient to cause the precipitation of sparingly soluble hydroxide of magnesium, zinc, manganese, etc., because their solubility product $[M^{++}]\times[OH^-]^2$ is low and is always exceeded. Thus zinc, manganese and magnesium are also precipitated along with $Fe(OH)_3$, $Cr(OH)_3$ and $Al(OH)_3$ in the third group.

If, however, we add excess of NH_4Cl to the salt solution before the addition of NH_4OH, ammonium chloride suppresses the ionization of ammonium hydroxide by common ion effect as explained above. The small OH^- concentration obtained after adding ammonium chloride to the solution is enough to precipitate hydroxides of iron, chromium and aluminium as their solubility products are very low.

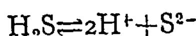
The new lower value of $[OH^-]$ is too low to precipitate zinc, manganese and magnesium hydroxides from their salt solutions as the ionic product $[M^{++}]\times[OH^-]$ does not exceed the solubility product.

This is the chemistry underlying Group III of qualitative analysis.

(*ii*) **Precipitation of Carbonates in Group V.** In the fifth group NH_4Cl is added before adding $(NH_4)_2CO_3$. This results in the suppression of $[CO_3^{2-}]$. The new low value of $[CO_3^{2-}]$ while sufficient to precipitate carbonates of barium, strontium and calcium, is not sufficient to cause precipitation of magnesium carbonate as its solubility product is not very low and is not exceeded when $[CO_3^{2-}]$ is very low due to the presence of NH_4Cl.

(*b*) **Precipitation of sulphides in the Second and Fourth Groups.** In qualitative analysis, the sulphides of Cu, Bi, Cd, Pb, Hg (*ic*), As, Sb and Sn are precipitated in the second group in presence of HCl, whereas those of Co, Ni, Zn and Mn are precipitated in the fourth group by H_2S in the presence of NH_4OH.

Hydrogen sulphide is a weak electrolyte which ionizes in solution as :

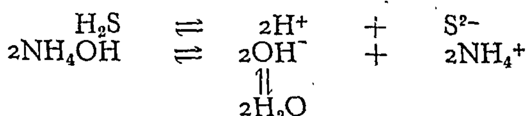


$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

In order that sulphide may be precipitated, the ionic product $[M^{2+}] \times [S^{2-}]$ must exceed its solubility product. The solubility products of the sulphides of second group are less than 1×10^{-28} whereas those of the fourth group far exceed this value (*e.g.*, for MnS it is 7×10^{-6}).

In presence of HCl, due to an increase in the concentration of H^+ ions, the ionization of H_2S is considerably suppressed due to the common ion effect. As a result of it the $[S^{2-}]$ as well as the ionic product $[M^{2+}][S^{2-}]$ are low. While this low ionic product cannot exceed the high solubility product of the sulphides of group IV, it exceeds the low solubility product of the sulphides of group II which are consequently precipitated in presence of HCl.

In order to precipitate the sulphides of group IV, it is essential to raise the ionic product. This is done by adding NH_4OH. H_2S and NH_4OH ionize as under :



$$\begin{array}{ccccc} H_2S & \rightleftharpoons & 2H^+ & + & S^{2-} \\ 2NH_4OH & \rightleftharpoons & 2OH^- & + & 2NH_4^+ \\ & & \upharpoons\downharpoons & & \\ & & 2H_2O & & \end{array}$$

The OH^- ions from NH_4OH combine with the H^+ ions from H_2S to form unionized water molecules with the result that more and more of H_2S ionizes. This causes an increase in $[S^{2-}]$ so much so that the high solubility product of the sulphides of Co, Ni, Mn and Zn is exceeded and they fall down as a precipitate.

(*c*) **Using Excess of Reagents in Quantitative Analysis.** Even insoluble substances have a solubility which, though very small, is measurable. In quantitative analysis we always add an excess of the precipitant so that the solubility product of the so-called insoluble substance is considerably exceeded and it is completely thrown out.

QUESTIONS

Essay-type Questions :

1. (a) Write a short note on the theory of ionization. What is the difference between an atom and an ion? How is this theory used to explain (a) neutralization; (b) electrolysis; and (c) the non-precipitation of zinc in Group II during analysis? *(Punjab Inter. 1960; U.P. 1960; Delhi H.S. 1961)*

(b) Distinguish between electrolytic dissociation and electrolysis. *(Delhi Pre-Medical 1964)*

(c) How does Theory of Ionization explain :

(i) The constant heat of neutralisation ;

(ii) The electrolysis of sodium hydroxide ? *(All-India H.S. 1966)*

2. How do solutions of acids, bases and salts differ from other solutions? How are these differences explained by a theory of ions? Why are the solutions of all salts not neutral to litmus? *(Punjab Pre-Univ. 1964)*

3. Give a brief account of the theory of Electrolytic Dissociation. Explain the terms acidity, alkalinity, neutralization and hydrolysis from the viewpoint of ionic hypothesis. *(Delhi Pre-Medical 1963, 60)*

4. Explain briefly the ionic hypothesis. How can you account for the phenomenon of (a) neutralization, (b) double decomposition, (c) alkaline reaction of potassium cyanide, (d) acidic reaction of an aqueous solution of ferric chloride, (e) precipitation, and (f) relative strengths of acids and bases. *(Madhya Pradesh Inter. 1964; Delhi H.S. 1954; All-India H.S. 1968; Delhi Pre-Medical 1963)*

5. Explain on the basis of Ionic Theory :

(a) The use of ammonium chloride in qualitative analysis.

(b) The alkalinity of a solution of sodium carbonate and acidity of a solution of ferric chloride.

(c) The precipitation of pure sodium chloride from a saturated solution of the impure salt by hydrochloric acid gas.

(d) Acid-base neutralization.

(e) Aqueous solution of $AlCl_3$ is acidic whereas that of NaCl is neutral. *(Punjab Pre-University, 1971, 70)*

6. Explain clearly why :

(a) A solution of sodium carbonate turns red litmus blue.

(b) The basic radical of a soluble salt does not interfere in the test of its acid radical and vice versa.

(c) Sodium chloride solution is a conductor of electricity.

(d) A solution of copper sulphate behaves acidic towards litmus.

(e) Pure chloroform does not give a white precipitate with silver nitrate solution.

(f) When dry hydrochloric acid gas is passed through concentrated brine, sodium chloride is precipitated. *(Punjab Inter. 1960)*

7. State the evidence on which the electrolytic dissociation theory is based. Explain two of the facts stated by you with the help of this theory.

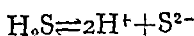
8. Write a short note on solubility product and its importance in qualitative analysis. *(Punjab Pre-Medical/Pre-Engg. T.D.C. Part I 1969)*

This is the chemistry underlying Group III of qualitative analysis.

(*ii*) **Precipitation of Carbonates in Group V.** In the fifth group NH_4Cl is added before adding $(NH_4)_2CO_3$. This results in the suppression of $[CO_3^{2-}]$. The new low value of $[CO_3^{2-}]$ while sufficient to precipitate carbonates of barium, strontium and calcium, is not sufficient to cause precipitation of magnesium carbonate as its solubility product is not very low and is not exceeded when $[CO_3^{2-}]$ is very low due to the presence of NH_4Cl.

(*b*) **Precipitation of sulphides in the Second and Fourth Groups.** In qualitative analysis, the sulphides of Cu, Bi, Cd, Pb, Hg (*ic*), As, Sb and Sn are precipitated in the second group in presence of HCl, whereas those of Co, Ni, Zn and Mn are precipitated in the fourth group by H_2S in the presence of NH_4OH.

Hydrogen sulphide is a weak electrolyte which ionizes in solution as :

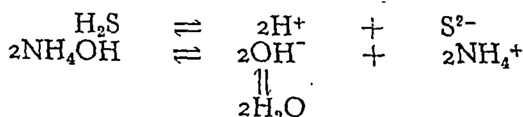


$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

In order that sulphide may be precipitated, the ionic product $[M^{2+}] \times [S^{2-}]$ must exceed its solubility product. The solubility products of the sulphides of second group are less than 1×10^{-28} whereas those of the fourth group far exceed this value (*e.g.*, for MnS it is 7×10^{-6}).

In presence of HCl, due to an increase in the concentration of H^+ ions, the ionization of H_2S is considerably suppressed due to the common ion effect. As a result of it the $[S^{2-}]$ as well as the ionic product $[M^{2+}][S^{2-}]$ are low. While this low ionic product cannot exceed the high solubility product of the sulphides of group IV, it exceeds the low solubility product of the sulphides of group II which are consequently precipitated in presence of HCl.

In order to precipitate the sulphides of group IV, it is essential to raise the ionic product. This is done by adding NH_4OH. H_2S and NH_4OH ionize as under :



$$\begin{array}{ccccc} H_2S & \rightleftharpoons & 2H^+ & + & S^{2-} \\ 2NH_4OH & \rightleftharpoons & 2OH^- & + & 2NH_4^+ \\ & & \upharpoons\downharpoons & & \\ & & 2H_2O & & \end{array}$$

The OH^- ions from NH_4OH combine with the H^+ ions from H_2S to form unionized water molecules with the result that more and more of H_2S ionizes. This causes an increase in $[S^{2-}]$ so much so that the high solubility product of the sulphides of Co, Ni, Mn and Zn is exceeded and they fall down as a precipitate.

(*c*) **Using Excess of Reagents in Quantitative Analysis.** Even insoluble substances have a solubility which, though very small, is measurable. In quantitative analysis we always add an excess of the precipitant so that the solubility product of the so-called insoluble substance is considerably exceeded and it is completely thrown out.

QUESTIONS

Essay-type Questions :

1. (*a*) Write a short note on the theory of ionization. What is the difference between an atom and an ion ? How is this theory used to explain (*a*) neutralization ; (*b*) electrolysis ; and (*c*) the non-precipitation of zinc in Group II during analysis ? (*Punjab Inter. 1960 ; U.P. 1960 ; Delhi H.S. 1961*)

(*b*) Distinguish between electrolytic dissociation and electrolysis. (*Delhi Pre-Medical 1964*)

(*c*) How does Theory of Ionization explain :

(i) The constant heat of neutralisation ;

(ii) The electrolysis of sodium hydroxide ? (*All India H.S. 1966*)

2. How do solutions of acids, bases and salts differ from other solutions ? How are these differences explained by a theory of ions ? Why are the solutions of all salts not neutral to litmus ? (*Punjab Pre-Univ. 1964*)

3. Give a brief account of the theory of Electrolytic Dissociation. Explain the terms acidity, alkalinity, neutralization and hydrolysis from the viewpoint of ionic hypothesis (*Delhi Pre-Medical 1963, 60*)

4. Explain briefly the ionic hypothesis. How can you account for the phenomenon of (*a*) neutralization, (*b*) double decomposition, (*c*) alkaline reaction of potassium cyanide, (*d*) acidic reaction of an aqueos solution of ferric chloride, (*e*) precipitation, and (*f*) relative strengths of acids and bases. (*Madhya Pradesh Inter 1964 ; Delhi H S. 1964 ; All-India H.S 1968 ; Delhi Pre-Medical 1963*)

5. Explain on the basis of Ionic Theory :

(*a*) The use of ammonium chloride in qualitative analysis.

(*b*) The alkalinity of a solution of sodium carbonate and acidity of a solution of ferric chloride.

(*c*) The precipitation of pure sodium chloride from a saturated solution of the impure salt by hydrochloric acid gas.

(*d*) Acid-base neutralization.

(*e*) Aqueous solution of $AlCl_3$ is acidic whereas that of NaCl is neutral. (*Punjab Pre-University, 1971, 72*)

6. Explain clearly why :

(*a*) A solution of sodium carbonate turns red litmus blue.

(*b*) The basic radical of a soluble salt does not interfere in the test of its acid radical and vice versa.

(*c*) Sodium chloride solution is a conductor of [illegible].

(*d*) A solution of copper sulphate behaves [illegible]

(*e*) Pure chloroform does not give a white [illegible] solution.

(*f*) When dry hydrochloric acid gas is passed [illegible] brine, sodium chloride is precipitated.

7. State the evidence on which the [illegible] is based. Explain two of the facts stated by you [illegible]

8. Write a short note on [illegible] qualitative analysis (*Punjab Pre-Medical* [illegible])

Test Your Understanding :

9. How does ionic theory explain the behaviour of acids and bases? Explain (*a*) why a solution of ferric chloride gives an acid reaction while that of sodium carbonate gives an alkaline reaction and (*b*) why a hydrogen more rapidly evolved when zinc is made to react with hydrochloric acid than with acetic acid of the same concentration? (*Delhi H.S. 1972*)

10. Fill in the blanks in the following :

(*i*) The electrolytes affect the freezing and boiling points of a solvent...

(*ii*) To explain the......behaviour of electrolytes,......proposed in 1887 his theory of......

(*iii*) Fraction of the total number of molecules ionised in a solution is termed......

(*iv*) Strength of an acid, base or salt depends upon its......

(*v*) Neutralization is the process of combination of......from an acid with......from a base to give unionised......

(*vi*) During electrolysis function of the electric current is to.............. already present in the solution, towards the oppositely charged......where they lose......and are liberated as......which may undergo......

(*vii*) Hydrolysis is the reaction of the anions (*e.g.*,......,......, etc.) of......with water to form......and the reaction of certain cations (*e.g.*,............., ...) with water to form......It is considered reverse of.......

(*viii*) Ionic product in a saturated solution of an electrolyte is called its.........

(*ix*) Precipitation of soap by adding common salts is termed ....

(*x*) Suppression of inoisation of NH_4OH by adding NH_4Cl is due to......

(*xi*) Addition of HCl......of H_2S by......in the II group of qualitative analysis.

(*xii*) Addition of NH_4Cl before adding $(NH_4)_2CO_3$ in the fifth group results in the suppression of [.........]

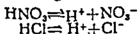
(*xiii*) If $[H^+]=1\times10^{-5}$ in a solution, it is ....(acidic/alkaline) and its pH......

KEY

(*i*) abnormally ; (*ii*) anomalous, Arrhenius, ionization ; (*iii*) degree of ionization ; (*iv*) degree of ionization ; (*v*) H^+, OH^-, water molecules; (*vi*) direct the ions, electrodes, their charge, atoms or radicals, secondary reactions ; (*vii*) F^-, CO_3^{2-}, weak acids ; OH^- ions , NH_4^+, Al^{3+}, Zn^{2+}, H^+ ions, neutralization ; (*viii*) solubility product ; (*ix*) salting out of soap ; (*x*) common ion effect ; (*xi*) suppresses the ionisation of, common ion effect ; (*xii*) CO_3^{2-} ; (*xiii*) acidic, 5.

Acids, Bases and Salts

1. Acids.—*Acids are substances containing hydrogen which in aqueous solution form no positive ions except hydrogen ions.* Most important acids are sulphuric acid, nitric acid and hydrochloric acid. A few other are acetic acid present in vinegar and lactic acid produced by souring of milk. Thus nitric acid and hydrochloric acid ionize as given below :



$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$
$$HCl \rightleftharpoons H^+ + Cl^-$$

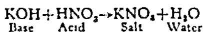
2. General Characteristics of Acids.—Common properties of acids as given below are in fact the properties of the hydrogen ions which all of them furnish in aqueous solution.

(*i*) All acids contain ionizable hydrogen and a *non-metallic* radical.

(*ii*) They have a sour taste.

(*iii*) They turn blue litmus red, methyl orange pink and decolorise phenolphthalein solution rendered pink with a drop of alkali.

(*iv*) Acids neutralize bases or basic oxides to produce salt and water, *e.g.*,



$$\underset{\text{Base}}{KOH} + \underset{\text{Acid}}{HNO_3} \rightarrow \underset{\text{Salt}}{KNO_3} + \underset{\text{Water}}{H_2O}$$

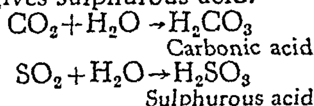
(*v*) They decompose carbonates when carbon dioxide is liberated with effervescence.

(*vi*) They act on some metals to liberate hydrogen, *e.g.*,

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

3. General Methods for Preparing Acids.—Different methods used for the preparation of acids are as follows :

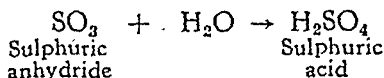
(1) **By the action of water on the oxide of a non-metal.** For example, *carbon dioxide dissolves in water to give carbonic acid*, sulphur dioxide gives sulphurous acid.



$$CO_2 + H_2O \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

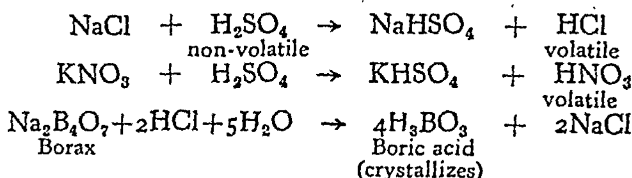
$$SO_2 + H_2O \rightarrow \underset{\text{Sulphurous acid}}{H_2SO_3}$$

Oxides of non-metals which combine with water to give acids are called **acid anhydrides.** Thus sulphur dioxide is the anhydride of sulphurous acid, sulphur trioxide is the anhydride of sulphuric acid.



$$\underset{\text{Sulphuric anhydride}}{SO_3} + H_2O \rightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$$

(2) **By decomposition of salts with other acids.** Volatile or insoluble acids can be prepared by the decomposition of their salts with other acids. The volatile hydrochloric and nitric acids are prepared by the decomposition of chlorides and nitrates respectively with non-volatile sulphuric acid. Similarly sparingly soluble boric acid is prepared by decomposition of borax with hydrochloric acid.



$$NaCl + \underset{\text{non-volatile}}{H_2SO_4} \rightarrow NaHSO_4 + \underset{\text{volatile}}{HCl}$$

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + \underset{\text{volatile}}{HNO_3}$$

$$\underset{\text{Borax}}{Na_2B_4O_7} + 2HCl + 5H_2O \rightarrow \underset{\text{Boric acid (crystallizes)}}{4H_3BO_3} + 2NaCl$$

(3) **By direct synthesis.** Hydrochloric acid is manufactured these days by burning hydrogen in an atmosphere of chlorine in specially designed burners.



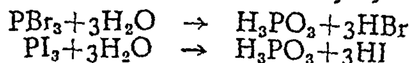
$$H_2 + Cl_2 \rightarrow 2HCl$$

Hydrobromic and hydriodic acids can be obtained by direct synthesis.



$$H_2 + Br_2 \rightarrow 2HBr$$

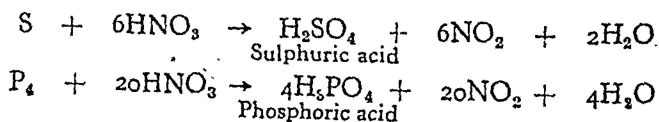
(4) **By hydrolysis of non-metal halides.** Hydrobromic and hydriodic acids are prepared in the laboratory by this method.



$$PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr$$

$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$$

(5) **By the oxidation of non-metals.** Concentrated nitric acid oxidises non-metals to their corresponding oxy-acids. For example, sulphur is oxidised to sulphuric acid and phosphorus to phosphoric acid.



$$S + 6HNO_3 \rightarrow \underset{\text{Sulphuric acid}}{H_2SO_4} + 6NO_2 + 2H_2O$$

$$P_4 + 20HNO_3 \rightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4} + 20NO_2 + 4H_2O$$

4. Nomenclature of Acids and their Salts.—Inorganic acids have been classified as hydracids, oxy-acids and thio-acids.

(*i*) Hydracids. These do not contain any oxygen. Their names begin with *hydro* and end in *ic* while their salts end in *ide*. For example,

Formula of the acid	Name of the acid	Salts named as
HCl	*Hydro*chlor*ic* acid	Chlor*ides*
HCN	*Hydro*cyan*ic* acid	Cyan*ides*
H_2S	*Hydro*sulphur*ic* acid	Sulph*ides*
HBr	*Hydro*brom*ic* acid	Brom*ides*

(ii) Oxy-acids. These contain oxygen as their essential constituent. Generally an element forms two oxy-acids. The name of the acid with lower proportion of oxygen ends in *ous* while that of the other with higher proportion of oxygen ends in *ic*. Their salts are named ending with *ites* and *ates* respectively. For example, in the case of acids of nitrogen and sulphur—

Formula of the acid	Name of the acid	Salts named as
HNO_2	Nitr*ous* acid	Nitr*ites*
HNO_3	Nitr*ic* acid	Nitr*ates*
H_2SO_3	Sulphur*ous* acid	Sulph*ites*
H_2SO_4	Sulphur*ic* acid	Sulph*ates*

In case an element gives more than two acids, these are indicated as *hypo—ous* and *per—ic* acids, while their salts are named as *hypo—ites* and *per—ates*. Thus in the case of four oxy-acids of chlorine—

Formula of the acid	Name of the acid	Salts named as
HClO	*Hypo*chlor*ous* acid	*Hypo*chlor*ites*
$HClO_2$	Chlor*ous* acid	Chlor*ites*
$HClO_3$	Chlor*ic* acid	Chlor*ates*
$HClO_4$	*Per*chlor*ic* acid	*Per*chlor*ates*

(iii) Thio-acids. These are derived from oxy-acids by [illegible] ms by sulphur atoms. The [illegible] t like oxy-acids and their

Oxy-acid	Thio-acid	Salts named as
H_2SO_4 Sulphuric acid	$H_2S_2O_3$ *Thiosulphuric* acid	*Thio*sulphates
HNCO Cyanic acid	HNCS *Thio*cyanic acid	*Thio*cyanates

5. **Basicity of an Acid.**—*Basicity of an acid is defined as the number of replaceable or ionizable hydrogen atoms contained in its one molecule.* Thus hydrochloric acid, HCl is *monobasic* or its basicity is one. Similarly sulphuric acid, H_2SO_4 and phosphoric acid, H_3PO_4 are *dibasic* (basicity=2) and *tribasic* (basicity=3) respectively.

6. **Bases.**—*Bases are substances containing hydroxyl groups which in aqueous solution form no negative ions other than OH^- ions.* For example, sodium hydroxide, potassium hydroxide, calcium hydroxide are common bases. They all give OH^- ions when dissolved in water.



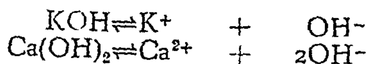
$$NaOH \rightleftharpoons Na^+ + OH^-$$

Acidity of a base *is the number of replaceable hydroxyl groups present in one molecule of the base.* For example, sodium hydroxide, NaOH and potassium hydroxide, KOH are monoacid bases while barium hydroxide, $Ba(OH)_2$ is di-acid base and aluminium hydroxide, $Al(OH)_3$ is a tri-acid one.

Those bases which are soluble in water are called **alkalis**, *e.g.*, caustic soda, NaOH and caustic potash, KOH.

7. **General Characteristics of Bases.**—Common properties of bases as given below are in fact properties of the OH^- ions.

(*i*) Bases contain a metal and one or more hydroxyl groups. They yield hydroxyl ions in solution.



$$KOH \rightleftharpoons K^+ + OH^-$$
$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

(*ii*) Soluble bases have a bitter taste.

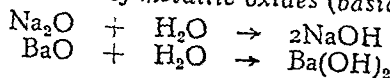
(*iii*) Solution of a base feels slippery to hand.

(*iv*) Soluble bases turn red litmus blue, phenolphthalein pink, methyl orange yellow and turmeric paper brown.

(*v*) They neutralize acids or oxides of non-metals (acidic oxides).

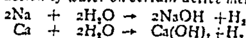
8. **Preparation of Bases.**—Different methods for the preparation of bases are :

(*i*) *By the action of metallic oxides (basic oxides) on water :*



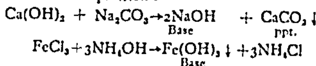
$$Na_2O + H_2O \rightarrow 2NaOH$$
$$BaO + H_2O \rightarrow Ba(OH)_2$$

(ii) *By the action of water on certain active metals :*



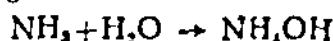
$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$
$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

(iii) *By double decomposition :*



$$Ca(OH)_2 + Na_2CO_3 \rightarrow \underset{\text{Base}}{2NaOH} + \underset{\text{ppt.}}{CaCO_3 \downarrow}$$
$$FeCl_3 + 3NH_4OH \rightarrow \underset{\text{Base}}{Fe(OH)_3 \downarrow} + 3NH_4Cl$$

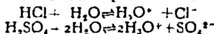
(iv) *By dissolving ammonia in water :*



$$NH_3 + H_2O \rightarrow NH_4OH$$

SOME MODERN CONCEPTS

9. **Hydrogen Ion.**—*Simple ionization of hydrogen atom by* loss of one electron would produce the hydrogen ion or proton but in water it is hydrated as the hydronium or hydroxonium ion H_3O^+. The hydronium ion occurs in all aqueous acidic solutions, *e.g.*,

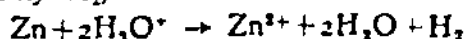


$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
$$H_2SO_4 + 2H_2O \rightleftharpoons 2H_3O^+ + SO_4^{2-}$$

Hydronium ion is responsible for the typical properties of acids, *e.g.*,

(i) It changes blue litmus red and methyl orange pink.

(ii) With more electropositive metals (*e.g.*, zinc, magnesium and iron) it liberates hydrogen.



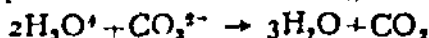
$$Zn + 2H_3O^+ \rightarrow Zn^{2+} + 2H_2O + H_2$$

(iii) Neutralization of bases can be represented as combination of hydronium ions with hydroxide ions to give water.



$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

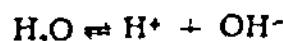
(iv) It decomposes carbonates liberating carbon dioxide.



$$2H_3O^+ + CO_3^{2-} \rightarrow 3H_2O + CO_2$$

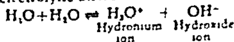
Although hydrogen ion is present in solution as solvated proton (hydronium ion), it is still common practice to refer to reactions of the hydrogen ion as involving the hydrogen ions. This *is entirely acceptable practice since solvation is normally neglected* with other ions.

10. **Acids and Bases.**—Water is a weak electrolyte and splits up slightly to form a positive hydrogen ion and a negative hydroxide ion.



$$H_2O \rightleftharpoons H^+ + OH^-$$

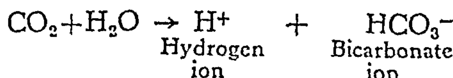
Each of these ions is hydrated. Perhaps a better way of describing this electrolytic dissociation is as follows .



$$H_2O + H_2O \rightleftharpoons \underset{\text{Hydronium ion}}{H_3O^+} + \underset{\text{Hydroxide ion}}{OH^-}$$

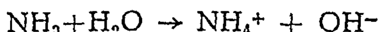
Substances can be added to water which upset the H^+—OH^- balance. Those substances *which increase the hydrogen-ion concentration* are called *acids* ; those substances *which increase the hydroxide-ion concentration* are called *bases.*

It may be useful to consider that hydrogen-ion increase can be brought about by substances like CO_2 which themselves do not contain any hydrogen.



$$CO_2 + H_2O \rightarrow \underset{\text{Hydrogen ion}}{H^+} + \underset{\text{Bicarbonate ion}}{HCO_3^-}$$

Similarly hydroxide-ion increase may be brought about by substances like NH_3 which themselves do not contain any hydroxyl group.



$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

According to **Bronsted-Lowry** definition, any proton donor is an acid and proton acceptor is a base. In the reaction between ammonium chloride and potassamide (KNH_2).

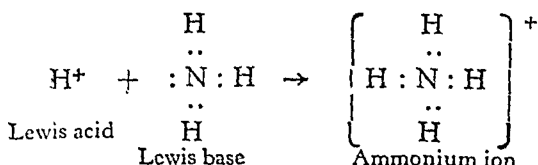


$$NH_4^+ + NH_2^- \rightarrow 2NH_3$$

NH_4^+ being a proton donor is an acid (Bronsted-Lowry acid) and NH_2 being a proton acceptor is a base (Bronsted-Lowry base).

Yet another commonly used definition of acid and base is due to **Lewis.** According to this, *acid is any species that acts as an electron-pair acceptor in chemical reaction. Similarly base is an electron-pair donor.*

For example, in the reaction

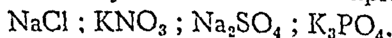


wherein H^+ accepts a pair of electrons from NH_3, H^+ is the Lewis acid and NH_3 is the Lewis base.

11. **Salts.**—*A salt is defined as a compound whose aqueous solution contains a positive ion other than H^+ and a negative ion other than OH^-.* The hydrogen and hydroxyl ions may also be present in addition to the other positive and negative ions which must be present.

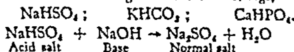
12. **Classification of Salts.**—Salts are further classified as :

(*i*) **Normal salts.** These contain neither replaceable hydrogen nor hydroxyl groups, *i.e.*, these are obtained by complete neutralization of a base by an acid. For example,



$$NaCl \; ; \; KNO_3 \; ; \; Na_2SO_4 \; ; \; K_3PO_4.$$

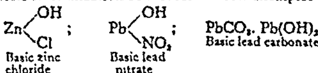
(ii) **Acid salts.** These contain some replaceable hydrogen and further react with a base to give normal salts, *e.g.*,



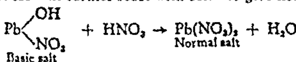
$$NaHSO_4\ ;\quad KHCO_3\ ;\quad CaHPO_4.$$

$$\underset{\text{Acid salt}}{NaHSO_4} + \underset{\text{Base}}{NaOH} \rightarrow \underset{\text{Normal salt}}{Na_2SO_4} + H_2O$$

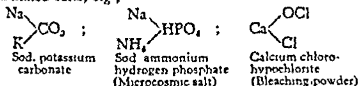
(iii) **Basic salts.** Salts which contain some replaceable hydroxyl groups are called basic salts. These are obtained by an incomplete neutralization of a base. A few examples are :



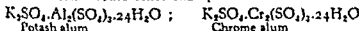
These will further react with acids to give normal salts.



(iv) **Mixed salts.** The salts which contain two distinct cations or anions other than hydrogen or hydroxyl groups are called mixed salts, e.g ,

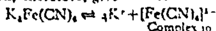


(v) **Double salts.** On concentrating a solution containing ferrous sulphate and ammonium sulphate, in equimolecular proportions, ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$ crystallizes out. Such salts formed by the union of two simple salts are called double salts. Some other examples are :



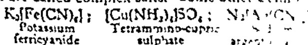
$$\underset{\text{Potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}\ ;\quad \underset{\text{Chrome alum}}{K_2SO_4.Cr_2(SO_4)_3.24H_2O}$$

(vi) **Complex salts.** Potassium ferrocyanide appears to be a double salt made up of potassium cyanide, and ferrous cyanide It behaves, however, entirely in a different manner when dissolved in water. Its solution gives no test for iron. Potassium ferrocyanide on dissolution in water breaks up into potassium ions and complex ferrocyanide ion. Iron is pre[illegible]t as a part of this complex ion and the solution, therefore, give[illegible] test for iron



$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + \underset{\text{Complex ion}}{[Fe(CN)_6]^{4-}}$$

Salts like potassium ferrocyanide which yiel[illegible] in solution are called complex salts. Some other exam[illegible]

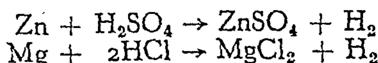


$$\underset{\text{Potassium ferricyanide}}{K_3[Fe(CN)_6]}\ ;\quad \underset{\text{Tetrammino-cupric sulphate}}{[Cu(NH_3)_4]SO_4}\ ;\quad [illegible]$$

13. **Preparation of Salts.**—Different methods employed are :

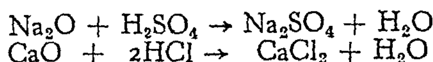
(a) *By the action of acids on :*

(i) METALS.



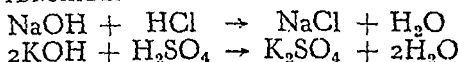
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

(ii) BASIC OXIDES.



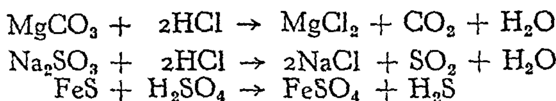
$$Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$$
$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

(iii) HYDROXIDES.



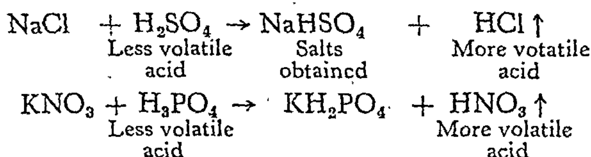
$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$$

(iv) CARBONATES, SULPHITES OR SULPHIDES.



$$MgCO_3 + 2HCl \rightarrow MgCl_2 + CO_2 + H_2O$$
$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O$$
$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

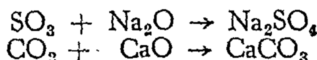
(v) SALTS OF VOLATILE ACIDS.



$$\underset{}{NaCl} + \underset{\text{Less volatile acid}}{H_2SO_4} \rightarrow \underset{\text{Salts obtained}}{NaHSO_4} + \underset{\text{More votatile acid}}{HCl\uparrow}$$
$$KNO_3 + \underset{\text{Less volatile acid}}{H_3PO_4} \rightarrow KH_2PO_4 + \underset{\text{More volatile acid}}{HNO_3\uparrow}$$

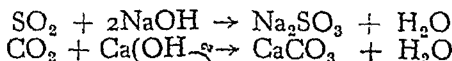
(b) *By the action of acidic oxides on :*

(i) BASIC OXIDES.



$$SO_3 + Na_2O \rightarrow Na_2SO_4$$
$$CO_2 + CaO \rightarrow CaCO_3$$

(ii) HYDROXIDES.



$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$$
$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

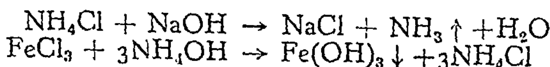
(iii) CARBONATES.



$$Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2$$

(c) *By the action of bases on :*

(i) SALTS.



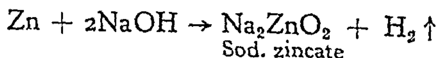
$$NH_4Cl + NaOH \rightarrow NaCl + NH_3\uparrow + H_2O$$
$$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3\downarrow + 3NH_4Cl$$

(ii) NON-METALS.



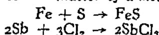
$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

(iii) METALS.



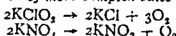
$$Zn + 2NaOH \rightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2\uparrow$$

(*d*) *By direct combination of a metal and a non-metal* :



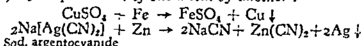
$$Fe + S \rightarrow FeS$$
$$2Sb + 3Cl_2 \rightarrow 2SbCl_3$$

(*e*) *Decomposition of more complex salts by heating* :



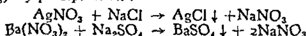
$$2KClO_3 \rightarrow 2KCl + 3O_2$$
$$2KNO_3 \rightarrow 2KNO_2 + O_2$$

(*f*) *By displacement of one metal by another* :



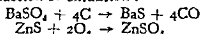
$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu\downarrow$$
$$\underset{\text{Sod. argentocyanide}}{2Na[Ag(CN)_2]} + Zn \rightarrow 2NaCN + Zn(CN)_2 + 2Ag\downarrow$$

(*g*) *By precipitation* :



$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$
$$Ba(NO_3)_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaNO_3$$

(*h*) *By reduction or oxidation* :



$$BaSO_4 + 4C \rightarrow BaS + 4CO$$
$$ZnS + 2O_2 \rightarrow ZnSO_4$$

14. **Properties of Salts.**—Salts are generally non-volatile, odourless soli... which ionize in solution. ... hydrolysis. Their solutio... litmus due to hydrolysis.

QUESTIONS

Essay-type Questions

1 (*a*) What is meant by the following terms :

(i) Acid. (ii) Base. (iii) Salt.

(*b*) Explain why an aqueous solution of $AlCl_3$ is acidic whereas an aqueous solution of NaCl is neutral. (*Punjab Pre-Univ. 1971*)

2 (*a*) What are salts and how are they classified ? Give examples.

(*b*) How will you distinguish between a normal salt and an acid salt. (*All-India H.S. 1968*)

3. Define the term acid, base and salt Illustrate a weak acid and a weak base. What types of salts are the following :

(i) Sodium bicarbonate , (ii) Potash alum ;
(iii) White lead ; (iv) Potassium ferrocyanide ;
(v) Sodium argentocyanide , (vi) Bleaching powder , and
(vii) Ferrous ammonium sulphate ? (*Delhi H S 1970, 65*)

4. Classify the following compounds as (i) acidic, (ii) basic and (iii) normal salts :

$NaHCO_3$, Na_2CO_3, NH_4Cl, $KClO_4$, $CuSO_4 \cdot 5H_2O$, NaClO, Pb(OH)Cl, $CuCO_3 \cdot Cu(OH)_2$ (*I I T. Admission Test 1969*)

5 Write short notes on .

(*a*) Acid salt.
(*b*) Acidity of a base.
(*c*) Basicity of an acid. (*All-India H.S. 19*

6. To what constituent do acids owe their characteristic properties? Does it impart these properties to all its compounds? What is the theory advanced to explain these facts? How do you explain the fact that some acids are stronger than others?

7. Give as many definitions of acids and bases as you can.

Test Your Understanding :

8. Fill in the blanks in the following :

(*i*) Acids are substances containing......which in aqueous solution form no......ion except......ions.

(*ii*) Basicity of a/an......is the number of ionizable......contained in its one molecule.

(*iii*) ......ion, H_3O^+ is responsible for the typical properties of......

(*iv*) Substances which increase the H_3O^+ ion concentration of water are called......others which increase OH^- ion concentration are termed......

(*v*) According to Bronsted-Lowry definition, any proton......is an acid and any proton......is a base.

(*vi*) According to Lewis acid is any species that acts as an electron pair......and base is any species that acts as an electron pair.........

(*vii*) A salt is a compound whose aqueous solution contains a positive ion other than......and a negative ion other than......and a negative ion other than......

9. Tick the correct answer :

A weak acid (*i*) does not affect litmus paper.

(*ii*) is always dibasic.

(*iii*) is insoluble in water.

(*iv*) will not react with NaOH solution.

(*v*) is only partly dissociated in solution.

KEY

8. (*i*) hydrogen, positive, H^+ ; (*ii*) acid, hydrogen atoms ; (*iii*) hydronium, acids ; (*iv*) acids, bases ; (*v*) donor, acceptor ; (*vi*) acceptor, donor ; (*vii*) H^+,OH^- ;

9. (*v*)

s-BLOCK ELEMENTS

GROUPS →

d-BLOCK ELEMENTS

p-BLOCK ELEMENTS

NOBLE GASES

PERIODS ↓

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn			As		Br	Kr
Rb	Sr									Ag	Cd			Sb		I	Xe
Cs	Ba									Au	Hg			Bi		At	Rn
	Ra																

24

MODERN PERIODIC TABLE

MODERN PERIODIC LAW ... OF ELEMENTS ... PERIODIC FUNCTION O[F] THEIR ATOMIC NUMBERS.

Classification of Elements

1. **Grouping of Elements into Families.**—The primary object of classification is to so arrange the known facts that we may learn the maximum possible of them with the least possible effort. It has been found convenient as well as possible to group elements into families, *e.g.*, alkali metals, halogens, noble gases, etc. In the study of alkali metals, if we study sodium in somewhat detail, the study of other members is found quite easy by comparison. In fact their chemical behaviour can be predicted with considerable accuracy. Similarly study of chlorine in detail facilitates the study of other halogens.

2. **Earlier A... ...ify Elements.**—Attempts we... and non-metals. It was fo... ...al nor the chemical properties of the elements are of such a nature as to make sharp division into two classes possible. Then there was another class of elements which possess the characteristics of both metals and non-metals. These are called metalloids.*

With the atomic theory having been placed on firm footing and following the determination of the atomic weights of a large number of elements with reasonable accuracy, attempts were made to classify elements on this basis, as given below :

(*a*) **Dobereiner's Triads.** As early as 1829, Dobereiner classified certain elements in groups of three, called *triads*. The three elements in a triad had similar properties and atomic weight

*For characteristics of metals and non-metals refer to Part III—METALS.

the middle element was an arithmetic mean of the atomic weights of the other two. For example,

Lithium	Sodium	Potassium
7	23	32

$$\text{Mean}=\frac{7+39}{2}=23.$$

Chlorine	Bromine	Iodine
35·5	80	127

$$\text{Mean}=\frac{35{\cdot}5+127}{2}=81{\cdot}25.$$

Only a limited number of elements could give such triads.

(*b*) **Newland's Law of Octaves.** In 1863, John A. Newland observed that if elements are arranged in the order of their atomic weights, *the eighth elements starting from a given one is a kind of repetition of the first like the eighth note of music.* Newland called it the Law of Octaves.

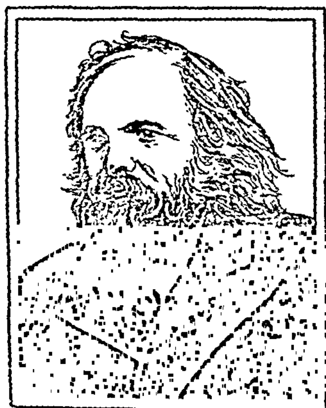
Li	Be	B	C	N	O	F
7	9	11	12	14	16	19
Na	Mg	Al	Si	P	S	Cl
23	24	27	28	31	32	35·5
K	Ca					
39	40					

Thus Na and K were a sort of repetition of Li and Cl was similar to F. The law broke down badly when applied beyond Ca. Also with the discovery of noble gases (Neon between F and Na ; Argon between Cl and K) it was the ninth element which was a repetition of the first, *i.e.*, the very idea of octave was lost.

(*c*) **Lothar Meyer's Graph.** Lothar Meyer (1869) plotted a graph between atomic weight and atomic volume of different elements. Similar elements were found by him to occupy similar positions on the curve.



Julius Lothar Meyer
(1830—45)
German chemist who was convinced that properties of elements are a periodic function of their atomic weights.



D. I. Mendeleeff
(1844—1907)
Russian chemist ; famous for his presentation of the periodic Law in 1869.

(*d*) **Mendeleeff's Periodic Law.** Russian chemist Mendeleeff (*men-deh-lay-eff*) stated in 1869 his famous periodic law—*Properties of elements are a periodic function of their atomic weights, i.e.*, if elements are arranged in the order of their atomic weights, similar elements are repeated at regular periods or intervals.

... known, in the order ... of a table called ...

(1) The nine vertical columns are called **Groups**. These, however, are not numbered 1 to 9, but 0 to 8. This is because members of Group 0 were not known when Mendeleeff compiled the original periodic table. These were discovered later on.

(2) Groups I to VII are sub-divided into **Sub-Groups**, A and B. Group VIII is the group of transitional elements and group 0 is the group of noble gases.

(3) The seven horizontal rows are called **Periods.**

Uses of Mendeleeff's Periodic Table. Mendeleeff's periodic table helped the chemists in the following ways :

(i) **Prediction of New Elements.** All vacant places in the table stand for new elements yet to be discovered. Their properties can be predicted from the properties of their neighbours. Thus Mendeleeff could predict with a fair degree of accuracy the properties of gallium and germanium called Eka-aluminium and Eka-silicon long before their discovery.

(ii) **Correction of Doubtful Atomic Weights.** Eq. wt. of beryllium was found to be 4·5 and from its sp. heat data its valency was found to be 3. This gave it the at. wt.$=4·5\times3=13·5$. With this atomic weight it could find no position between C $(=12)$ and N $(=14)$. Hence valency two was assigned to it which gave it the at. wt.$=9$ and it was assigned a place between Lithium and Boron. At. wt. of Indium was corrected in a similar manner.

Main Defects in the Periodic Table. (1) **Position of hydroge**... halogens is not clear. ... ion while like halide ... be placed both in I and VII groups.

(2) **Some similar elements separated and dissimilar elements grouped together.** Certain chemically similar elements, *e.g.*, copper and mercury or gold and platinum, are placed in different groups while some other dissimilar elements are grouped together. For example, alkali metals, copper, silver and gold have been placed in the same group though they are dissimilar.

---

* A modern and the modified form of the periodic table is given on page 1·236 and includes the elements discovered since that time.

PERIODIC TABLE (*Modified form of Mendeleeff's Table*)

PERIODS	Group :	I A	I B	II A	II B	III A	III B	IV A	IV B	V A	V B	VI A	VI B	VII A	VII B	VIII	Zero
	Oxide : Hydride :	R_2O RH		RO RH_2		R_2O_3 RH_3		RO_2 RH_4		R_2O_5 RH_3		RO_3 RH_2		R_2O_7 RH		RO_4 Transition Triads	Noble gases
1		H 1 (At.No.) 1·008 (At.Wt.)															He 2 4·0036
2		Li 3 6·939		Be 4 9·012		B 5 10·81		C 6 12·011		N 7 14·007		O 8 15·999		F 9 18·998			Ne 10 20·183
3		Na 11 22·99		Mg 12 24·31		Al 13 26·98		Si 14 28·09		P 15 30·974		S 16 32·06		Cl 17 35·453			Ar 18 39·948
4	First series	K 19 39·102		Ca 20 40·08			Sc 21 44·96		Ti 22 47·90		V 23 50·94		Cr 24 52·20		Mn 25 54·94	Fe 26 Co 27 Ni 28 55·85 58·93 58·71	
	Second series		Cu 29 63·54		Zn 30 65·37	Ga 31 69·72		Ge 32 72·59		As 33 74·92		Se 34 78·96		Br 35 79·909			Kr 36 83·80
5	First series	Rb 37 85·47		Sr 38 87·62			Y 39 88·91		Zr 40 91·22		Nb 41 92·91		Mo 42 95·94		Tc 43 (99)	Ru 44 Rh 45 Pd 46 101·07 102·91 106·4	
	Second series		Ag 47 107·87		Cd 48 112·40	In 49 114·82		Sn 50 118·69		Sb 51 121·75		Te 52 127·60		I 53 126·90			Xe 54 131·30
6	First series	Cs 55 132·90		Ba 56 137·34			Rare Earths 57 - 71		Hf 72 178·49		Ta 73 180·95		W 74 183·85		Re 75 186·2	Os 76 Ir 77 Pt 78 190·2 192·2 195·09	
	Second series		Au 79 196·97		Hg 80 200·59	Tl 81 204·37		Pb 82 207·19		Bi 83 208·98		Po 84 (210)		At 85 (210)			Rn 86 (222)
7		Fr 87 (223)		Ra 88 (226)	Eka Hg 112		Actinide Elements 89—103		Ku 104		Ha 105		...		...	... ...	

Lanthanide Elements (*Rare earth series*)	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
	138·91	140·12	140·91	144·24	(145)	150·35	151·96	157·2,	158·92	162·50	164·93	167·26	168·93	173·03	174·97
Actinide Series	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103
	(227)	232·04	(231)	238·73	(237)	(244)	(247)	(245)	(247)	(249)	(254)	(252)	(256)	(254)	(257)

(3) Rare Earths. A group of [illegible] rare earths, do not find their proper places in the table and are all put together in one position.

(4) Anomalous Pairs of Elements. Certain elements of higher atomic weight precede others with lower atomic weight as given below :

Argon (At. [illegible] (At. wt.=39·1)
Cobalt (At. [illegible] (At. wt.=58·6)
Tellurium (At. [illegible] (At. wt.=126·9)

(5) Position of Isotopes. A large number of isotopes of different elements do not find any room in the periodic table.

3. Modern Periodic Law.—As a result of the modern researches it is established that atomic number and not the atomic weight is a fundamental property of the atom. This led Moseley to change the basis of classification of elements from atomic weight to atomic number. The modern periodic law as given by Moseley can be stated as follows :

The properties of elements are a periodic function of their atomic numbers, i e., if elements can be arranged in the order of their atomic numbers, similar elements are repeated after regular intervals.

With this change in the basis of classification the defects (4) and (5) disappear. The various anomalous pairs are found to occupy their proper places while different isotopes of the same element (their atomic numbers being identical) do not require separate positions.

Element	Ar	K	Co	Ni	Te	I
At. No.	18	19	27	28	52	53

4. Periodic Nature of Valency.—The periodic law is based on the periodic nature of valency. The number of valency electrons in the outermost orbit of an element determines its valency and we find that the same number of valency electrons are periodically repeated as illustrated below in the case of alkali metals and halogens.

ALKALI METALS		HALOGENS	
Lithium,	Li 2, 1	Fluorine,	F 2, 7
Sodium,	Na 2, 8, 1	Chlorine,	Cl 2, 8, 7
Potassium,	K 2, 8, 8, 1	Bromine,	Br 2, 8, 18, 7
Rubidium,	Rb 2, 8, 18, 8, 1	Iodine,	I 2, 8, 18, 18, 7
Caesium,	Cs 2, 8, 18, 18, 8, 1	Astatine	At 2, 8, 18, 32, 18, 7
Francium,	Fr 2, 8, 18, 32, 18, 1		
	(Valency Electron=1)		*(Valency Electrons=7)*

MODERN PERIODIC TABLE (*Extended Form*)

Group → / Period	IA	II A	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
	Active metals		Transition Metals								Cu–Zn Group		Metalloids and Non-metals					
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi. 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac† 89	Ku 104	Ha 105													
												Eka-mercury 112						

*Lanthanide Elements	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
†Actinide Series	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

Thus we find that all alkali metals possess one valency electron and are, therefore, monovalent electropositive while halogens with seven valency electrons are all monovalent electronegative. Same is the case with other normal elements.

It is seen that elements with the same number of valency electrons are repeated at regular intervals and they resemble each other. This is periodic law.

5. *Modern Trends in Periodic Classification* —With the shift of basis from at. wt. to atomic number as cause of periodicity a large number of modified charts and models have been suggested. Most useful of these modifications and at the same time easiest also is the so-called long or Bohr's table given on page 1·238 in its modern form.

The main features of the long table can be summarized as follows:

(1) In this table there are 16 vertical columns called sub-groups. These are numbered IA, IB, IIA, IIB, ..., VIIA, VIIB, VIII and 0.

(2) Elements of sub-groups IA, IIA, ..., VIIA have only outermost shells incomplete. Each one of their inner shells is complete. These are called **Normal elements.**

(3) Elements of sub-groups IB, IIB, ..., VIIB and VIII have their outermost as well as the penultimate shell incomplete. These are termed **Transition elements.**

(4) Elements of sub-group 0 have all their shells complete. These do not show any reactivity and are termed **Noble gases.**

(5) Horizontal rows are called periods. There are seven periods in the table.

(*i*) The first periods is of 2 elements (H—He).

(*ii*) Second and third are two *short periods* of 8 elements each (Li—Ne and Na—Ar).

(*iii*) Fourth and fifth are *long periods* of 18 elements each (K—Kr and Rb—Xe) while sixth is a long period of 32 elements (Cs—Rn) including rare earth elements (At. No. 57 - 71) which are all placed in the same group in the table.

(*iv*) Seventh is an incomplete period of 19 elements which are radioactive. Elements with atomic number 93—105 are only synthetic elements discovered during atomic research. Another heavy element with At. No.=112 has been reported and named Eka mercury for the present.



Gleun Theore Seaburg
(1912—)
American physical chemist; he is famous for his research on the transuranic elements (At. No. 93—105).

(6) In this the long periods have been extended and the short periods broken so as to accommodate the transitional elements in the long periods at their proper places.

(7) The noble gases have been grouped at the extreme right of the table.

(8) The lanthanides and the actinides have been grouped separately and placed at the bottom.

The long form of the periodic table has more clarity than the Mendeleeff's periodic table in the following respects :

(1) It is based upon a more fundamental base, *i.e.*, Atomic numbers.

(2) It relates the position of an element to the electronic arrangement in its atoms and is, therefore, nearly an ideal arrangement.

(3) It reflects the similarities, differences and trends in chemical properties more clearly.

(4) It is an easy chart to remember and to reproduce.

(5) There is a logical separation of sub-groups in it. The elements found in any of its vertical columns resemble closely with one another.

(6) The divisions indicated in the table—active metals, transition metals, copper-zinc group, metalloids and non-metals, rare-earth metals (Lanthanide elements), radioactive metals (Actinide series) represent the major groups.

(7) There is no chance of erroneous conclusions being drawn which often results from the Mendeleeff's system.

(8) The meaning of transitional elements is more clearly understood and their place in a long period is justified in the light of their electronic configuration. These are elements with their penultimate shells incomplete.

Some Horizontal, Vertical and Diagonal Relationships in the Periodic Table.

(1) **Valency Electrons.** Number of valency electrons increases from 1 to 8 on moving horizontally across a period. On moving down a group the number of valency electrons does not change.

(2) **Valency.** In each short period valency with respect to hydrogen increases from one to four and then falls again to one while with respect to oxygen, it increases from one to seven.

Valency with respect to hydrogen (Elements of the first short period)

Group	I	II	III	IV	V	VI	VII
Valency	1	2	3	4	3	2	1
Hybrides	LiH	—	BH_3	CH_4	NH_3	H_2O	HF
Chlorides	LiCl	$BeCl_2$	BCl_3	CCl_4	NCl_3	Cl_2O	ClF

Valency with respect to oxygen (Elements of the first short period).

Group	I	II	III	IV	V	VI	VII
Valency	1	2	3	4	5	6	7
Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7

In the same sub-group all the elements have the same valency.

Group number is the valency of the element with respect to oxygen.

(3) **Properties of Elements.** Elements in the same sub-group resemble each other. For example, members of the sub-group IA—Li, Na, K, Rb, Cs, Fr are alkali metals and resemble each other.

There is a regular gradation in the properties of elements in the same sub-group, *e.g.*, base forming tendency increases from Li to Cs in group IA. Similarly reactivity decreases as we pass from fluorine (F) to iodine (I) in group VIIA. There is a regular gradation in their physical constants like m.p., b.p., density, etc.

Elements in the II short period—Na, Mg, etc. are called Typical Elements since each one of them is a typical representative of its group.

(4) **Size of Atoms and Ions.** *Size of the atoms decreases from left to right across a period,* in the periodic table. Thus in any period alkali metal is the largest atom and the halogen the smallest.

The size of the atoms increases on descending a group in the periodic table. For example, in sub-group IA atomic size increases steadily from lithium to caesium.

A positive ion is smaller than the corresponding atom, whereas negative ions are bigger than the corresponding atoms.

(5) **Ionization Potential.** The firmness with which an electron is held by an atom is a measure of its ionization potential. It is defined as the energy required to pull off an electron from the atom, *i.e.*, energy required for the reaction $X \rightarrow X^{+} + e^{-}$.

In the Bo[illegible]
potential occur [illegible]
the left of the ta[illegible]
of the ionization potential in going from top to bottom.

(6) **Electronegativity.** *The tendency of an atom in a compound to attract electrons towards itself is termed the electronegativity of the atom.*

In general, small atoms attract electrons more than large ones and [illegible] nearly filled [illegible] higher elec-

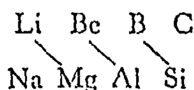
Electronegativity increses from left to right across a period and decreases as we descend a group.

(7) **Metallic Character.** On moving from left to right across a period the metallic character of the elements decreases and their oxides become less and less basic. For example,

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Strongly basic	basic	amphoteric	feebly acidic	acidic	more acidic	most acidic

On descending a vertical group in the periodic table, the metallic character increases. This is particularly apparent in Groups IVA and VA which begin with the non-metals, carbon and nitrogen, and end with the metals, lead and bismuth respectively. Their oxides become increasingly basic.

(8) **Diagonal Relationship.** On moving diagonally across the periodic table the elements show certain similarities. These are usually weaker than the similarities within a group but are quite pronounced in the case of a few elements given below :



This can be more clearly understood in the light of change of electronegativity across a period and on descending a group. Electronegativity increases as we move from left to right across a period and decreases as we descend a group.

Starting from lithium and moving one step to the right brings up to beryllium with a little higher electronegativity than lithium. Moving one step down from beryllium brings us to magnesium with a little lower electronegativity than beryllium. We might, therefore, expect lithium and magnesium to have the same values of electronegativity both having a little less electronegativity than beryllium. Having equal electronegativity lithium and magnesium resemble each other in a number of respects (*Diagonal relationship*).

The line separating the metals from non-metals also runs diagonally.

10. A Brief Survey of the Horizontal, Vertical and Diagonal Relationships in the Periodic Table.

(*a*) *On moving horizontally across a period :*

(*i*) Number of valency electrons (electrons in the outermost shell) increases from one to eight.

(*ii*) In short periods valency with respect to hydrogen increases from 1 to 4 and then decreases to 1. With respect to oxygen it increases from 1 to 7.

(*iii*) Size of the atoms decreases.

(*iv*) Ionization potential increases.

(*v*) Metallic character decreases and the basic nature of their oxides decreases.

(*vi*) Electronegativity increases.

(*b*) *On descending a vertical group* :

(*i*) All the atoms have the same number of valency electrons.

(*ii*) All the elements have the same valency.

(*iii*) Elements resemble each other and there is a regular gradation in their physical constants and chemical properties.

(iv) Size of the atoms increases.

(*v*) Ionization potential decreases.

(*vi*) Metallic character increases and the basic nature of their oxides increases.

(*vii*) Electronegativity decreases.

(*c*) *On moving diagonally across the periodic table* :

(*i*) Elements show certain similarities (*Diagonal relationship*).

(*ii*) Diagonal similarities are most important among the lighter *elements.*

(*iii*) The line separating the metals from the non-metals also run diagonally.

QUESTIONS

Essay-type Questions ·

1. Write a short account of the periodic classification of elements. State the advantages and anomalies of the classification (*U P. Board Inter. 1960; Kashmir 1962, Delhi Pre-Medical 1963, 61 ; Punjab H.S. 1963, Delhi H S 1963, 61*)

2. *Write an essay on the various attempts at the classification of* elements leading to the Periodic Table in all its details. State the periodic law.

3. (*a*) State periodic law. How did it help in the discovery of new elements ? (*Delhi Pre-Medical 1961*)

(*b*) Write a short note on Periodic Law. (*All-India H.S. 1968*)

4 State modern periodic law. Draw a sketch of the long table and give its main features In what respects the long form of the periodic table has more clarity than the Mendeleeff's table.

5. Discuss various horizontal, vertical and diagonal reactions in the periodic table.

6. State and explain Mendeleeff's *Periodic Law. How has this been* modified ? How has the periodic table been useful for the study of chemistry ? (*Delhi H.S. 1966*)

7 What are the main features of the Periodic Table ? Discuss its importance. (*All-India H S. 1967*)

8. How does the Periodic Table help in the systematic study of Chemistry ? In what way is the long form of the periodic table better than Mendeleeff's Table ? (*Punjab Pre-Univ. 1970*)

Test Your Understanding :

9. Write a detailed account of the Periodic classification of elements. (*Delhi H.S. 1972*)

10. Give an outline of the Long form of the periodic table. Fill in this the elements of sub-groups IA, VA, VIIA and those of the two short periods and one long period.

How do the metallic character and valency change along a group and along a period ? (*Delhi Pre-Medical 1972*)

11. (*a*) Arrange in the order of increasing ionization potentials :

(*i*) Elements of group IA.

(*ii*) Elements of the II period (Li to F).

(*b*) Arrange in order of increasing atomic size :

(*i*) Ca, Sr and Ba ; (*ii*) Li, Na and K.

(*c*) Which are the transition elements in the Periodic Table ? How ar they characterised in terms of electronic configuration ?

(*d*) What is the name given to the relationship which explains simila propeties of Li and Mg ? Name two more pairs which show this relationship.

KEY

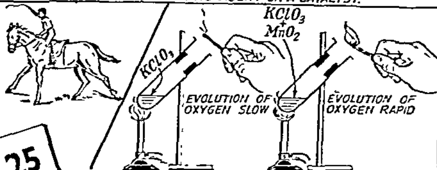
(*a*) (*i*) Fr, Cs, Rb, K, Na, Li,

(*ii*) Li, Be, B, C, N, O, F.

(*b*) (*i*) Ca, Sr, Ba ; (*ii*) Li, Na, K

(*c*) Elements of groups IB, IIB......, VIIB. Their outermost as well a the penultimate shells are incomplete.

(*d*) Diagonal relationship ; Be and Al ; B and Si.



Catalysis

1. What is Catalysis.—Heat some potassium chlorate in a test tube. It has to be heated much above its melting point before it decomposes to give oxygen and the evolution of the gas is still slow. Now heat a mixture of potassium chlorate and manganese dioxide in another test tube. Decomposition starts at much below its melting point with rapid evolution of oxygen. Manganese dioxide is found to remain unchanged at the end of chemical reaction. *A substance of the kind of manganese dioxide, which by its mere presence increases (or sometimes decreases) the rate of a chemical action without itself being permanently changed is called a* catalytic agent or a catalyst. *The action of a catalyst in changing the rate at which a chemical reaction proceeds is called* catalysis.

2. Types of Catalysis.—(i) Positive Catalysis. A catalyst may accelerate or retard a chemical reaction. It is called a *positive catalyst* when it increases the rate of reaction while the process is termed *positive catalysis*. Manganese dioxide used above and platinised asbestos used in the contact process for the manufacture of sulphuric acid are examples of positive catalysis.

(ii) Negative Catalysis. Catalysts employed to decrease the velocity of a chemical reaction are called *negative catalysts* and the action is known as *negative catalysis*. Phosphoric acid retards the decomposition of hydrogen peroxide and oxidation of chloroform is slower in presence of alcohol. These are instances of negative catalysis.

(iii) **Autocatalysis.** In certain reactions one of the products of reaction acts as a catalyst for that reaction. This is known as *Auto-catalysis.* For example,

(*a*) Reaction between nitric acid and copper is slow in the beginning but gains speed gradually and is quite brisk after some time. Here nitrous acid is one of the products of reaction which accelerates the reaction.

(*b*) The reaction between potassium permanganate and oxalic acid in presence of dilute sulphuric acid is also slow in the beginning and becomes brisk after some time. Here manganous sulphate is one of the products of reaction which accelerates the chemical reaction.

(*iv*) **Induced Catalysis.** In certain cases there is no substance which acts as a catalytic agent, one of the reactions induces the other reaction. For example, sodium arsenite is not oxidised by air but sodium sulphite is oxidised by air. If air is passed through their mixture, oxidation of sodium sulphite induces the oxidation of sodium arsenite also. The phenomenon in which one reaction induces another reaction is called *Induced Catalysis.*

3. **Characteristics of Catalytic Reactions.**—(*i*) *The catalyst does not undergo any change in mass and composition as a result of the chemical reaction.* It may, however, undergo a physical change *e.g.*, during the decomposition of potassium chlorate manganese dioxide is found to have changed from a coarse powder to a fine one at the end of the reaction.

(*ii*) *A very small quantity of the catalyst is needed to accelerate a chemical reaction.*

(*iii*) *It does not alter the position of equilibrium in a reversible reaction.* As the catalyst accelerates both the forward and the backward reactions to the same extent, the equilibrium point remains unaltered. *A catalyst simply helps in the quick attainment of the equilibrium state, e.g.,* function of catalyst in a reversible endothermic reaction is to reach the equilibrium point quickly at the temperature favourable for the reaction.

(*iv*) *A catalyst cannot start a reaction but only alters the speed of the reaction.* Some experiments, however, seem to contradict the statement, *e.g.*, perfectly dry nitric oxide and oxygen fail to react. Presence of traces of moisture, which acts as a catalyst in the reactions, is necessary to start these reactions.

(*v*) *The action of catalyst is specific.* Just as a particular key can open only one particular lock, a certain catalyst can accelerate only one definite reaction.

(*vi*) *In some cases the efficiency of a catalyst is enhanced by the presence of some other substance called* **promoter** *or* **activator**. A promoter by itself cannot catalyse a chemical action. Thus in the Haber's process for the manufacture of ammonia, *molybdenum* is a promoter used with the catalyst, finely divided iron.

(*iii*) *The catalysts lose their efficiency in the presence of substances known as* catalyst poisons. Common poisons are carbon monoxide and arsenious oxide. Thus during the manufacture of sulphuric acid by Contact Process, traces of As_2O_3 poison the catalyst, platinised asbestos.

4. **Mechanism of Catalysis.**—There are two theories commonly used to explain the working of the catalyst. These are :

(*i*) **Intermediate Compound Formation Theory.** In a given number of molecules at a specified temperature, some have [illegible] gy-rich molecules as com- [illegible] rcentage of molecules are [illegible] normal energy.
[illegible] sult of collision between reacting molecules, possessing sufficiently high energy to react. Molecules with normal energy simply collide and rebound without reacting. *The extra energy which the two molecules must possess in order to react is termed the* activation energy *of the reaction.*

In the absence of the catalyst since the activation energy of the reaction is high, the reaction takes place only between small fraction of molecules with high energy and the reaction is quite slow. In the presence of a catalyst the activation energy of the reaction is comparatively lower and even molecules with lower energy can react. Hence more of the molecules participate in the reaction which takes place faster.

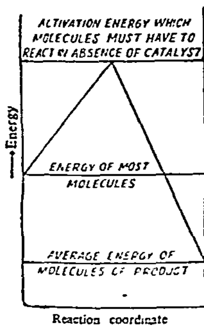


Fig. 25·1 (a)—An exothermic reaction requiring high energy molecules, proceeds slowly.

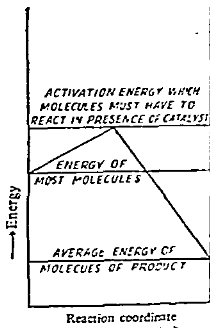


Fig 25·1 (b)—A catalyst lowers the activation energy enabling more molecules to participate in the reaction.

The role of a catalyst may be explained on the basis of the following analogy :

If a mountainous road leads directly up and across, only cars with extremely powerful engines can go up the road and complete the journey. However, if the road leads through a tunnel in the mountain provided at half the height or less, all the cars can go over.

The catalyst makes the molecules with normal energy react by forming an intermediate compound. Two substances A and B which do not react directly do so in the presence of a catalyst C. At first the catalyst combines with one of the reactants A to give an intermediate compound AC. This reacts further with the second reactant B to form the final product AB regenerating the catalyst C.

(i) $A + B \longrightarrow AB$ (*very slow reaction*)

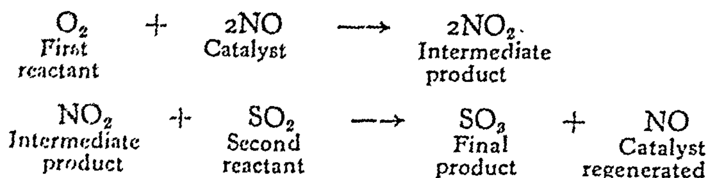
Activation energy of the reaction being high, AB is formed very slowly.

(ii) $A + \underset{\text{Catalyst}}{C} \longrightarrow \underset{\text{Intermediate product}}{AC}$ (*rapid*)

(iii) $\underset{\text{Intermediate product}}{AC} + \underset{\text{Second reactant}}{B} \longrightarrow \underset{\text{Final product}}{AB} + \underset{\text{Catalyst regenerated}}{C}$ (*rapid*)

Activation energies of the two reactions being low, both these reactions are fast and AB is formed rapidly.

Action of nitric oxide catalyst in the Lead Chamber Process for the manufacture of sulphuric acid is explained by the Intermediate Compound formation theory.



$$\underset{\text{First reactant}}{O_2} + \underset{\text{Catalyst}}{2NO} \longrightarrow \underset{\text{Intermediate product}}{2NO_2}$$

$$\underset{\text{Intermediate product}}{NO_2} + \underset{\text{Second reactant}}{SO_2} \longrightarrow \underset{\text{Final product}}{SO_3} + \underset{\text{Catalyst regenerated}}{NO}$$

(ii) **Adsorption Theory.** Many solid substances have the property of holding appreciable quantities of liquids and gases *on their surface*. The gas or liquid molecules do not penetrate the interior of the solid. The phenomenon is referred to as adsorption. Finely divided solids like nickel and platinum are known for their ability to adsorb large amounts of gases due to their larger surface area.

In the *Adsorption Theory* the catalyst is supposed to adsorb the reactants on its surface. The adsorbed molecules are frequently more reactive than the unadsorbed molecules. This increased reactivity is attributed to one of the following factors :

(i) Due to increased concentration of the adsorbed molecules which are crowded close together on the catalyst surface.

(ii) The attractive forces between the molecules of the solid and those of the adsorbed gas or liquid make the adsorbed molecules more reactive chemically.

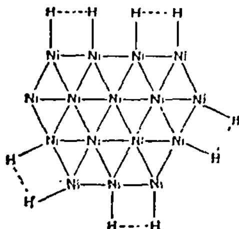


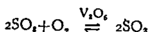
Fig. 25·2—A cross-section diagram of a tiny nickel crystal showing adsorbed hydrogen. In this the strong covalent bond that joins two hydrogen atoms is either weakened or broken. Thus hydrogen adsorbed on a nickel catalyst is much more active than the unadsorbed hydrogen.

This causes the reaction between molecules A and B to take place on the surface of the solid at a faster rate. As the reaction proceeds the products leave the surface and more reactants are adsorbed.

Action of finely divided metals as catalyst is explained in terms of adsorption.

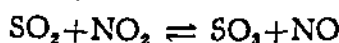
5. Applications of Catalysts.—A few examples of the many applications of catalysts in the chemical industries are given below :

(i) **Manufacture of Sulphuric Acid.**—Sulphur dioxide is oxidised to sulphur trioxide in the presence of platinised asbestos or vanadium pentaoxide (catalyst) in the Contact Process.



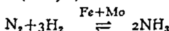
$$2SO_2+O_2 \overset{V_2O_5}{\rightleftharpoons} 2SO_3$$

In the Chamber Process the oxidation is effected in the presence of oxides of nitrogen.



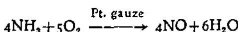
$$SO_2+NO_2 \rightleftharpoons SO_3+NO$$

(ii) **Synthesis of Ammonia.** In the Haber's Process, nitrogen and hydrogen combine to give ammonia in the presence of finely divided iron (catalyst) and a little molybdenum (promoter).



$$N_2+3H_2 \overset{Fe+Mo}{\rightleftharpoons} 2NH_3$$

(iii) **Ostwald's Process for Nitric Acid.** This is based on the catalytic oxidation of ammonia in the presence of platinum gauze at 800°C as a catalyst.

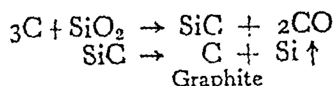


$$4NH_3+5O_2 \xrightarrow{\text{Pt. gauze}} 4NO+6H_2O$$

(iv) **Hydrogenation of Oils.**—*Vanaspati ghee* is manufactured by hydrogenation of oils in the presence of finely divided nickel as a catalyst.

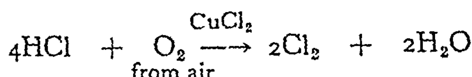
Unsaturated esters (*oils*)$+H_2\rightarrow$Saturated esters (*fats*).

(*v*) **Manufacture of Graphite.** In the Acheson Process for the manufacture of graphite by heating anthracite and sand, the latter acts as a catalyst.



$$3C + SiO_2 \rightarrow SiC + 2CO$$
$$SiC \rightarrow \underset{\text{Graphite}}{C} + Si\uparrow$$

(*vi*) **Deacon's process for the Manufacture of Chlorine.** Here hydrochloric acid gas is oxidised by atmospheric oxygen in the presence of pumice stone soaked in cupric chloride.



$$4HCl + \underset{\text{from air}}{O_2} \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

6. **Important Catalysts.**—Some important catalysts commonly used are :

(A) FINELY DIVIDED METALS

(*i*) **Nickel.** Used in hydrogenation of oils and other unsaturated organic compounds.

(*ii*) **Iron.** Used in the Haber's Process for the manufacture of ammonia.

(*iii*) **Platinum.** Used as finely divided platinum deposited in asbestos in the Contact Process for the manufacture of sulphuric acid.

(B) WATER VAPOUR

Perfectly dry gases do not react chemically. Thus traces of water vapour act as a general catalyst in gaseous reactions.



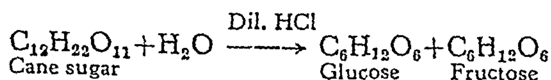
$$NH_3 + HCl \xrightarrow{\text{Moisture}} NH_4Cl$$



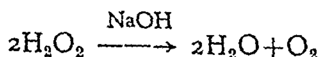
$$H_2 + Cl_2 \xrightarrow{\text{Moisture}} 2HCl$$

(C) ACIDS AND ALKALIS

Dilute acids catalyse the inversion of cane sugar or hydrolysis of esters. Presence of alkalis accelerates the decomposition of hydrogen peroxide while acids retard it.



$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Dil. HCl}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$



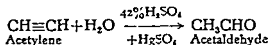
$$2H_2O_2 \xrightarrow{NaOH} 2H_2O + O_2$$

(D) COMPOUNDS EASILY OXIDISED OR REDUCED

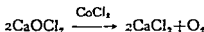
(*i*) **Cupric chloride.** Used in the Deacon's Process for the manufacture of chlorine.

(*ii*) **Oxides of nitrogen.** Used in the Chamber Process for the manufacture of sulphuric acid.

(*iii*) **Mercuric sulphate.** With 42% sulphuric acid, mercuric sulphate is used to convert acetylene to acetaldehyde in organic synthesis.

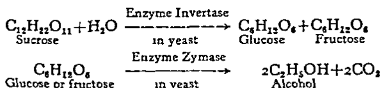

$$\underset{\text{Acetylene}}{CH\equiv CH+H_2O} \xrightarrow[+HgSO_4]{42\%H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(*iv*) **Cobalt chloride.** It catalyses the decomposition of bleaching powder.


$$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2+O_2$$

(E) ENZYMES

Organic reactions carried out in the presence of living ferments are catalysed by non-living nitrogenous substances called enzymes.


$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}+H_2O} \xrightarrow[\text{in yeast}]{\text{Enzyme Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$
$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Enzyme Zymase}} \underset{\text{Alcohol}}{2C_2H_5OH}+2CO_2$$

QUESTIONS

Essay-type Questions :

1. How many of the following terms can you define or explain ?

Catalysis	Catalytic agent	Auto-catalysis
Promoter	Positive catalyst	Induced catalysis
Activator	Negative catalyst	Catalytic poisons

2. Explain the meaning of the term Negative Catalysis. What part does manganese dioxide play in the preparation of oxygen from potassium chlorate ?

Outline briefly how ammonia and sulphur trioxide are manufactured by means of catalysis. (Delhi H S. 1960)

3. Write a short note on 'Catalysis'. (*Delhi H.S. 1964, 62*)

4. Write an essay on Catalysis and its applications in chemical industry. (*All-India H S. 1967, Delhi H S. 1960*)

5. Name the catalysts used in the preparation of : (i) NH_3 from N_2 and H_2, (ii) NO from ammonia and air, (iii) ethane from ethylene and hydrogen ; (*iv*) ethyl alcohol from cane sugar. (*I I.T Admission Test 1971*)

6. Explain 'Catalysis'. Name four catalytic agents and mention their application in the manufacture of important substances (*Punjab Pre-Medical/Pre-Engg./B Sc I Year 1964*)

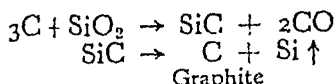
7. Write a short essay on catalytic agents touching on the following points :

(*a*) Mode of behaviour of catalysts (*b*) Poisoning of catalysts.

(*c*) Illustration of catalytic action in any three industrial processes. (*Delhi H.S. 1966*)

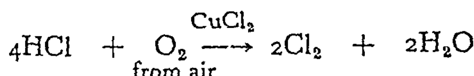
8. Write a short note on Mechanism of Catalysis. (*Delhi Pre-Medical 1971*

(*v*) **Manufacture of Graphite.** In the Acheson Process for the manufacture of graphite by heating anthracite and sand, the latter acts as a catalyst.



$$3C + SiO_2 \rightarrow SiC + 2CO$$
$$SiC \rightarrow \underset{\text{Graphite}}{C} + Si\uparrow$$

(*vi*) **Deacon's process for the Manufacture of Chlorine.** Here hydrochloric acid gas is oxidised by atmospheric oxygen in the presence of pumice stone soaked in cupric chloride.



$$4HCl + \underset{\text{from air}}{O_2} \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

6. **Important Catalysts.**—Some important catalysts commonly used are :

(A) FINELY DIVIDED METALS

(*i*) **Nickel.** Used in hydrogenation of oils and other unsaturated organic compounds.

(*ii*) **Iron.** Used in the Haber's Process for the manufacture of ammonia.

(*iii*) **Platinum.** Used as finely divided platinum deposited in asbestos in the Contact Process for the manufacture of sulphuric acid.

(B) WATER VAPOUR

Perfectly dry gases do not react chemically. Thus traces of water vapour act as a general catalyst in gaseous reactions.



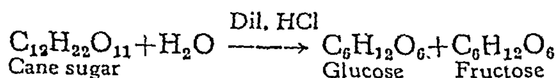
$$NH_3 + HCl \xrightarrow{\text{Moisture}} NH_4Cl$$



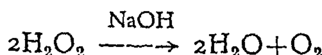
$$H_2 + Cl_2 \xrightarrow{\text{Moisture}} 2HCl$$

(C) ACIDS AND ALKALIS

Dilute acids catalyse the inversion of cane sugar or hydrolysis of esters. Presence of alkalis accelerates the decomposition of hydrogen peroxide while acids retard it.



$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Dil. HCl}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$



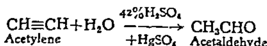
$$2H_2O_2 \xrightarrow{NaOH} 2H_2O + O_2$$

(D) COMPOUNDS EASILY OXIDISED OR REDUCED

(*i*) **Cupric chloride.** Used in the Deacon's Process for the manufacture of chlorine.

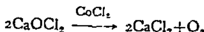
(*ii*) **Oxides of nitrogen.** Used in the Chamber Process for the manufacture of sulphuric acid.

(*iii*) **Mercuric sulphate.** With 42% sulphuric acid, mercuric sulphate is used to convert acetylene to acetaldehyde in organic synthesis.



$$\underset{\text{Acetylene}}{CH\equiv CH}+H_2O \xrightarrow[+HgSO_4]{42\%H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

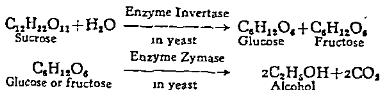
(*iv*) **Cobalt chloride.** It catalyses the decomposition of bleaching powder.



$$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2+O_2$$

(E) ENZYMES

Organic reactions carried out in the presence of living ferments are catalysed by non-living nitrogenous substances called enzymes.



$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}}+H_2O \xrightarrow[\text{in yeast}]{\text{Enzyme Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6}+\underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Enzyme Zymase}} \underset{\text{Alcohol}}{2C_2H_5OH}+2CO_2$$

QUESTIONS

Essay-type Questions.

1. How many of the following terms can you define or explain ?

Catalysis	Catalytic agent	Auto-catalysis
Promoter	Positive catalyst	Induced catalysis
Activator	Negative catalyst	Catalytic poisons

2. Explain the meaning of the term Negative Catalysis. What part does manganese dioxide play in the preparation of oxygen from potassium chlorate ?

Outline briefly how ammonia and sulphur trioxide are manufactured by means of catalysis. *(Delhi H.S. 1960)*

3. Write a short note on 'Catalysis' *(Delhi H.S. 1964, 62)*

4. Write an essay on Catalysis and its applications in chemical industry. *(All-India H.S. 1957 ; Delhi H.S. 1960)*

5. Name the catalysts used in the preparation of : (i) NH_3 from N_2 and H_2, (ii) NO from ammonia and air ; (iii) ethane from ethylene and hydrogen ; (iv) ethyl alcohol from cane sugar. *(I I T. Admission Test 1971)*

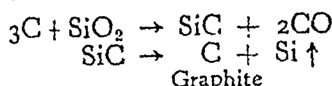
6. Explain 'Catalysis'. Name four catalytic agents and mention their application in the manufacture of important substances. *(Punjab Pre-Medical Pre-Engg B.Sc I Year 1964)*

7. Write a short essay on catalytic agents touching on the following points :

(*a*) Mode of behaviour of catalysts. (*b*) Poisoning of catalysts.
(*c*) Illustration of catalytic action in any three industrial processes. *(Delhi H.S. 1956)*

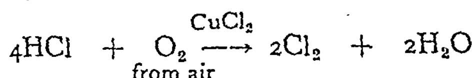
8. Write a short note on Mechanism of Catalysis. *(Delhi Pre-Medical 19—)*

(*v*) **Manufacture of Graphite.** In the Acheson Process for the manufacture of graphite by heating anthracite and sand, the latter acts as a catalyst.



$$3C + SiO_2 \rightarrow SiC + 2CO$$
$$SiC \rightarrow \underset{\text{Graphite}}{C} + Si\uparrow$$

(*vi*) **Deacon's process for the Manufacture of Chlorine.** Here hydrochloric acid gas is oxidised by atmospheric oxygen in the presence of pumice stone soaked in cupric chloride.



$$4HCl + \underset{\text{from air}}{O_2} \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

6. **Important Catalysts.**—Some important catalysts commonly used are :

(A) FINELY DIVIDED METALS

(*i*) **Nickel.** Used in hydrogenation of oils and other unsaturated organic compounds.

(*ii*) **Iron.** Used in the Haber's Process for the manufacture of ammonia.

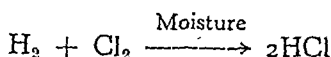
(*iii*) **Platinum.** Used as finely divided platinum deposited in asbestos in the Contact Process for the manufacture of sulphuric acid.

(B) WATER VAPOUR

Perfectly dry gases do not react chemically. Thus traces of water vapour act as a general catalyst in gaseous reactions.



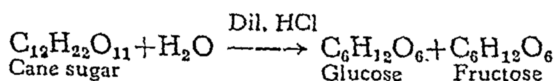
$$NH_3 + HCl \xrightarrow{\text{Moisture}} NH_4Cl$$



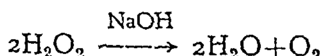
$$H_2 + Cl_2 \xrightarrow{\text{Moisture}} 2HCl$$

(C) ACIDS AND ALKALIS

Dilute acids catalyse the inversion of cane sugar or hydrolysis of esters. Presence of alkalis accelerates the decomposition of hydrogen peroxide while acids retard it.



$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Dil. HCl}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$



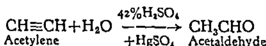
$$2H_2O_2 \xrightarrow{NaOH} 2H_2O + O_2$$

(D) COMPOUNDS EASILY OXIDISED OR REDUCED

(*i*) **Cupric chloride.** Used in the Deacon's Process for the manufacture of chlorine.

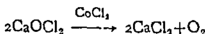
(*ii*) **Oxides of nitrogen.** Used in the Chamber Process for the manufacture of sulphuric acid.

(iii) **Mercuric sulphate.** With 42% sulphuric acid, mercuric sulphate is used to convert acetylene to acetaldehyde in organic synthesis.



$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \xrightarrow[+HgSO_4]{42\%H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

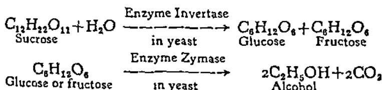
(iv) **Cobalt chloride.** It catalyses the decomposition of bleaching powder.



$$2CaOCl_2 \xrightarrow{CoCl_2} 2CaCl_2 + O_2$$

(E) ENZYMES

Organic reactions carried out in the presence of living ferments are catalysed by non-living nitrogenous substances called enzymes.



$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{in yeast}]{\text{Enzyme Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow[\text{in yeast}]{\text{Enzyme Zymase}} \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2$$

QUESTIONS

Essay-type Questions :

1. How many of the following terms can you define or explain ?

Catalysis	Catalytic agent	Auto-catalysis
Promoter	Positive catalyst	Induced catalysis
Activator	Negative catalyst	Catalytic poisons

2. Explain the meaning of the term Negative Catalysis. What part does manganese dioxide play in the preparation of oxygen from potassium chlorate ?

Outline briefly how ammonia and sulphur trioxide are manufactured by means of catalysis.
(*Delhi H.S. 1960*)

3. Write a short note on 'Catalysis'. (*Delhi H.S. 1964, 62*)

4. Write an essay on Catalysis and its applications in chemical industry.
(*All-India H S 1967 ; Delhi H S. 1960*)

5. Name the catalysts used in the preparation of : (i) NH_3 from N_2 and H_2, (ii) NO from ammonia and air ; (iii) ethane from ethylene and hydrogen ; (iv) ethyl alcohol from cane sugar. (*I.I.T. Admission Test 1971*)

6. Explain 'Catalysis'. Name four catalytic agents and mention their application in the manufacture of important substances.
(*Punjab Pre-Medical/Pre-Engg /B.Sc. I Year 1964*)

7. Write a short essay on catalytic agents touching on the following points

(a) Mode of behaviour of catalysts. (b) Poisoning of catalysts.
(c) Illustration of catalytic action in any three industrial processes.
(*Delhi H.S. 1966*)

8. Write a short note on Mechanism of Catalysis.
(*Delhi Pre-Medical 1971*)

9. What are the chief characteristics of a Catalyst ? Discuss briefly the various theories that have been put forward to explain the phenomenon of Catalysts. *(Delhi Pre-Medical 1972)*

Test Your Understanding :

10. Fill in the blanks in the following :

(*i*) A substance of the kind of......which by its mere presence increases (or decreases) the rate of a chemical action without itself being permanently changed is called......

(*ii*) A positive catalyst is one which......the velocity of reaction whereas a negative catalyst is one which.........the velocity of reaction.

(*iii*) Efficiency of a catalyst is enhanced by the presence of another substance called......or......

(*iv*) The catalysts lose their efficiency in the presence of substances known as......

(*v*) The extra energy which the two molecules must possess in order to react is termed......

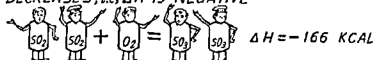
(*vi*) In the presence of a catalyst......of the reaction is comparatively ......and even molecules with lower energy can react.

(*vii*) Action of nitric oxide catalyst in Lead chamber process is explained by the......theory whereas action of finely divided metals as catalyst is explained in terms of......theory.

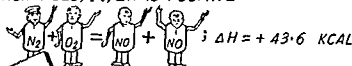
KEY

(*i*) dioxide, a manganese catalytic agent ; (*ii*) increases, decreases ; (*iii*) promoter, activator ; (*iv*) catalyst poisons ; (*v*) activation energy ; (*vi*) activation energy, lower ; (*vii*) Intermediate compound formation, adsorption.

FOR AN EXOTHERMIC REACTION, ENTHALPY OF A SYSTEM DECREASES, i.e, ΔH IS NEGATIVE



FOR AN ENDOTHERMIC REACTION ENTHALPY OF A SYSTEM INCREASES, i.e, ΔH IS POSITIVE



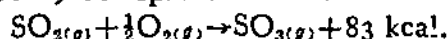
26

WHEN ATOMS COMBINE TO GIVE MOLECULES, ENERGY IS ABSORBED AND STORED AS BOND ENERGY WHICH IS RELEASED WHEN THE BONDS BREAK

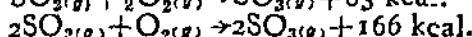
Energy Changes in Chemical Reactions

1. **Heat Changes during Chemical Reactions.**—It is common knowledge that some kind of energy (heat, light or electricity) is either used up or evolved in a chemical reaction. Thus when gaseous sulphur dioxide and oxygen react, under certain conditions, to form gaseous sulphur trioxide, 83 kcal. of heat *per mole* of sulphur trioxide formed are evolved.

The reaction may be represented as :

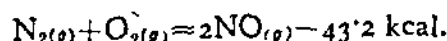

$$SO_{2(g)}+\tfrac{1}{2}O_{2(g)}\rightarrow SO_{3(g)}+83 \text{ kcal.}$$

or

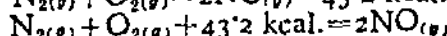

$$2SO_{2(g)}+O_{2(g)}\rightarrow 2SO_{3(g)}+166 \text{ kcal.}$$

Such a reaction is known as *exothermic reaction*. Formation of ammonia from nitrogen and hydrogen and of water from hydrogen and oxygen are other examples of *Exothermic reaction*.

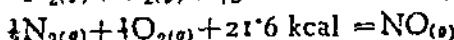
When nitrogen and oxygen mixture is passed through an electric arc, nitric oxide is formed. Heat is absorbed in the formation of nitric oxide. *Reactions in which heat is absorbed are known as Endothermic Reactions.*


$$N_{2(g)}+O_{2(g)}=2NO_{(g)}-43{\cdot}2 \text{ kcal.}$$

or


$$N_{2(g)}+O_{2(g)}+43{\cdot}2 \text{ kcal.}=2NO_{(g)}$$

or


$$\tfrac{1}{2}N_{2(g)}+\tfrac{1}{2}O_{2(g)}+21{\cdot}6 \text{ kcal}=NO_{(g)}$$

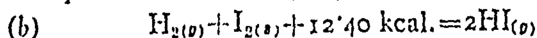
In *the above case 21·6 kcal. of heat is absorbed* for *one mole of nitric oxide gas produced* from half a mole each of nitrogen and oxygen, both gaseous.

Some other examples of endothermic reactions are :

(a)


$$C_{(s)}+2S_{(s)}+28 \text{ kcal.}=CS_{2(l)}$$

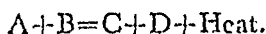
One mole of carbon atoms in the solid state combine with two moles of sulphur atoms, also in the solid state and absorb 28 kcal. of heat to produce one mole of liquid carbon disulphide.



(b) $H_{2(g)} + I_{2(s)} + 12{\cdot}40$ kcal. $= 2HI_{(g)}$

One mole of gaseous hydrogen and one mole of solid iodine absorb 12·4 kcal. of heat to produce two moles of gaseous hydrogen iodide.

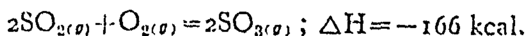
Heat is a form of energy. It means energy *changes take place during chemical reactions.* In an exothermic reaction, heat is evolved, so that products must have lower energy than the reactants. In the same manner in an endothermic reaction the products must have more energy than the reactants. Thus during *an exothermic reaction there is a decrease in the heat content of the substances while in an endothermic reaction there is an increase in the heat content of the substances.* Symbol H is used to indicate **heat content** or **enthalpy** of a system. Consider the reaction



$$A + B = C + D + \text{Heat.}$$

Suppose heat content of reactants A and B taken together is H_1 and that of products C and D taken together is H_2. Because heat is evolved in the above reaction, so final heat content of the system, H_2, must be less than initial heat content of the system, H_1 or $H_2 - H_1$ is a negative quantity. $H_2 - H_1$ represents the change in the heat content (or enthalpy of the system) and is represented as ΔH. So ΔH in an exothermic reaction (or change in enthalpy of an exothermic reaction) is negative. In the same manner change in enthalpy of an endothermic reaction is positive. These enthalpy changes are represented as shown below :

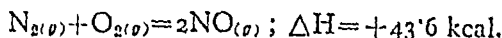
(i) *An exothermic reaction :*



$$2SO_{2(g)} + O_{2(g)} = 2SO_{3(g)}\ ;\ \Delta H = -166 \text{ kcal.}$$

Hence ΔH or change in enthalpy, is negative and heat is evolved in the reaction.

(ii) *An endothermic reaction :*



$$N_{2(g)} + O_{2(g)} = 2NO_{(g)}\ ;\ \Delta H = +43{\cdot}6 \text{ kcal.}$$

In this case ΔH is positive and heat is absorbed in the reaction.

2. **Heat Content.**—We have been talking about heat content of substances, but what is the actual significance of the term ? When coal is burnt in oxygen we get carbon dioxide and 94·0 kcal. of heat are evolved for one mole of the gas formed.



$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + 94{\cdot}0 \text{ kcal.}$$

This 94·0 kcal. is a fixed amount and is always formed by burning of one mole of solid coal atoms. It cannot be varied at our whims. We conclude that one mole of coal and one mole of oxygen have definite energy associated with them and the formation of carbon

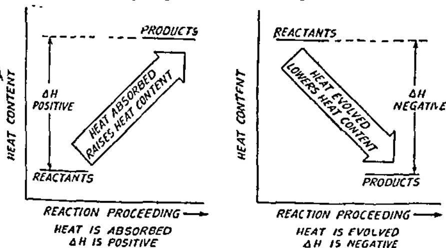
dioxide results in a compound with lesser *energy*. The difference in energy is given out as heat. Or we might say that the *heat content* of the products is less than that of reactants in this case.

Heat Content *measures the energy stored in a substance during its formation. The heat effect in a chemical reaction measures the difference between the heat contents of the products and the heat content of the reactants.* If more energy is stored in the reactants than in products, then heat will be released during the reaction. Conversely, heat will be absorbed if more energy is stored in the products than in the reactants. The difference in the heat content of the products and reactants is called ΔH.

$$\Delta H = \begin{bmatrix}\text{Heat content}\\ \text{of product}\end{bmatrix} - \begin{bmatrix}\text{Heat content}\\ \text{of reactants}\end{bmatrix}$$

It is positive when heat content is rising by heat absorption (*endothermic reaction*) and it is negative when heat content is dropping by heat evolution (*exothermic reaction*).

The following diagram will make the point clear :

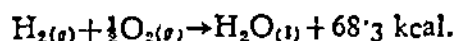


[Endothermic Reaction] [Exothermic Reaction]

Fig 26·1—Heat content change during a reaction.

3. **Energy and its Conservation.**—It has been pointed out above when a definite quantity of substance *A* reacts with a definite quantity of *B* to produce *C* and *D*, the heat change taking place is fixed. It amounts to saying *that the reactants and products have definite energies associated with them and the difference in these manifests itself in the form of heat change. Or the energy of a system is always conserved.* Can this be experimentally proved ?

[illegible] a calorimeter [illegible] (by noting the ris[illegible] on gases), we conclude



$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} + 68{\cdot}3 \text{ kcal.}$$

It means the heat content of hydrogen and oxygen in the above case is less than that of water by 68·3 kcal. If we supply an energy

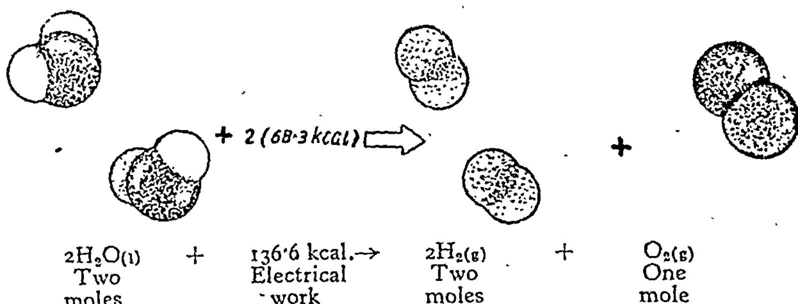


Fig. 26·2 (*a*)—Conservation of Energy in a Chemical Reaction.

equivalent to this, in a suitable form, it should be possible for us to get from one mole of liquid water. a mole of hydrogen gas and half a mole of oxygen gas, if the law of conservation of energy is true. Water can be decomposed to hydrogen and oxygen by electric current (doing electric work). It has been found that *electrical work*

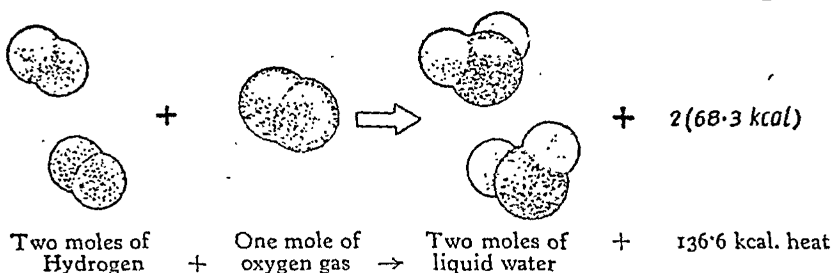


Fig. 26·2 (*b*) –Conservation of Energy in a Chemical Reaction.

equivalent to 68·3 kcal. of heat is required to decompose one mole of liquid water into its constituents. This work has been *stored* in the two gases and is *released* when they are made to interact. *Thus*

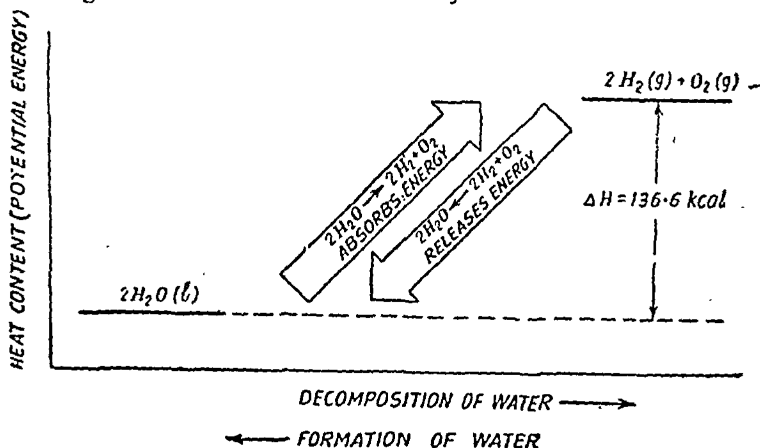


Fig. 26·3—Energy change in a Chemical Reaction.

energy is conserved at all times. Substances (hydrogen and oxygen in the above case) have the capacity to store energy. This capacity to store energy is also termed *heat content.* When substances interact the energy is conserved *provided all* the *different forms of energy are taken into consideration.* Countless experiments have been performed and the law has been found to be valid. If a characteristic heat content is assigned to each substance, then all of these experiments support the Law of Conservation of Energy. *Law of Heat Summation* (discussed later) based on the assumption of Conservation of Energy has been found to be valid in hundreds of reactions studied so far.

4. Energy Stored in Molecules.—It has been suggested above that energy is stored in molecules of substances and when molecules react to form new molecules by rearrangement of atoms, energy changes take place as the new combinations of atoms may have different capacities of storing energy. The question arises, how is this energy stored in molecules (and in atoms)?

We are aware of different types of energy at the *macroscopic* level—at the level of weighable and visible quantities like—

(1) *Kinetic energy, e.g.*, energy of a moving cricket ball.

(2) *Potential energy, e.g.*, energy of a football at the height of its flight when kicked high.

(3) *Heat energy, e.g.*, the energy in steam used in running a steam engine.

(4) *Heat content or Chemical energy.* The atoms of a molecule are 'bound' together by certain forces—the forces represented by various chemical bonds in the molecule. This is termed as the *chemical bond energy* of the molecule. Different bonds have different energies associated with them as is clear from the fact that different energies are needed to break different bonds. Thus to break the bonds between hydrogen atoms in H_2 molecules require an energy of *104·2 kcal. for one mole of molecules* while to break Cl—Cl bonds in one mole of chlorine only 58·0 kcal. of energy are needed.

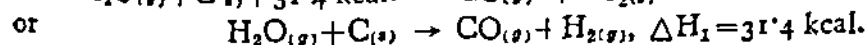
(5) *Electrical energy, e.g.*, energy used in electrolysing acidulated water, etc.

...scopic level all the macro-
...f only two kinds
...ergy.

5. Hess's Law.—When steam is passed over heated coke water gas is produced and the thermochemical equation can be written as:



$$H_2O_{(g)} + C_{(s)} + 31{\cdot}4 \text{ kcal.} \rightarrow CO_{(g)} + H_{2(g)}$$

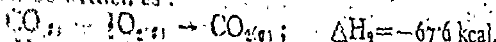


or $$H_2O_{(g)} + C_{(s)} \rightarrow CO_{(g)} + H_{2(g)},\ \Delta H_1 = 31{\cdot}4 \text{ kcal.}$$

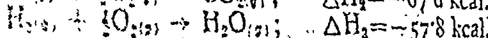
I
case i



In the same way burning of carbon monoxide in oxygen to produce carbon dioxide and burning of hydrogen in oxygen to produce water can be written as :

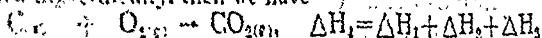


$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}; \quad \Delta H_2 = -67.6 \text{ kcal.}$$

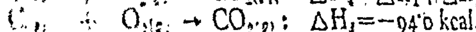


$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}; \quad \Delta H_3 = -57.8 \text{ kcal.}$$

The first reaction is an endothermic reaction while the last two reactions are exothermic ones. If the above three equations are added algebraically, then we have



$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}, \quad \Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$$



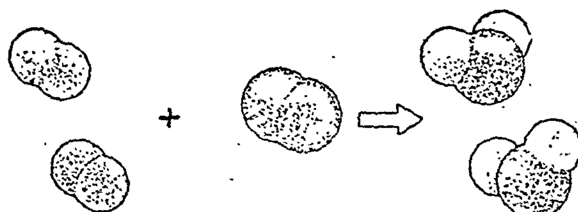
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}: \quad \Delta H_4 = -94.0 \text{ kcal.}$$

$2H_2O_{(l)}$ Two moles + 136·6 Electrical work ... the algebraic sum + ΔH_2 and ΔH_3 is equal to ... of one mole of carbon

Fig. 26·2 (a)—Conservation of Energy in a Chemical R...

equivalent to this, in a suitable form, it should be pos... kcal.
get from one mole of liquid water, a mole of hydroge... 94·0 kcal.
a mole of oxygen gas, if the law of conservation of ene... ressed as the alge-
Water can be decomposed to hydrogen and oxygen... reactions, the heat
current (doing electric work). It has been found that ele... s of these reactions.

...aw of Heat Sum-
...n Heats.
...few terms we come
...c and exothermic



...is the change in
...ecules of the re-
...pletely reacted

Fig. 26·2 (b) —Conservation of Energy in a Chemical Reaction

equivalent to 68·3 kcal. of heat is required to decompose one ... of liquid water into its constituents. This work has been *sto*... the two gases and is *released* when they are made to interact.

...f an elemen... ...en 1 gram ...rbon, Δ ... a co... ...of t... ...ecc...

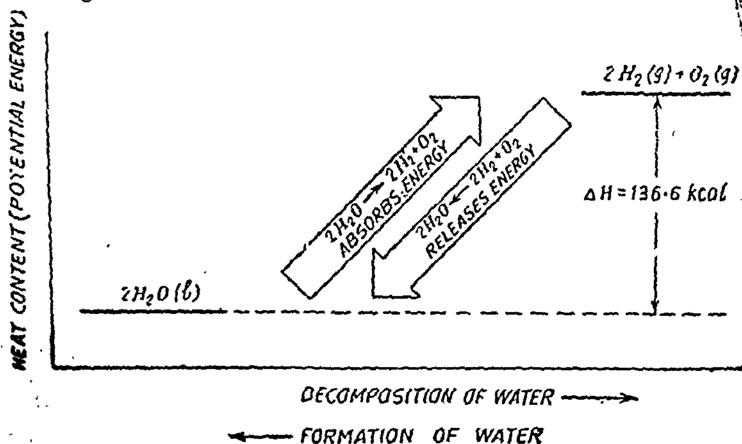


Fig. 26·3—Energy change in a Chemical Reaction.

UESTIONS

ıd by the following terms :

ı,

ction,

Enthalpy.

ange in an exothermic reaction ?

t forms is energy stored in molecules ? What is
ıd energy, and (ii) Molecular heat content.

rt note on Hess's law of heat summation.

4. Ex... the terms :

(i) Heat of reaction,

(ii) Heat of combustion,

(iii) Heat of formation.

5. Fill in the blanks :

(1) If heat is evolved in a reaction, the temperature will........ Such ...ns are termed........ reactions.

(2) If heat is.........in a reaction, the temperature will fall. Such reactions ...med.........reactions.

(3) Write the equation $A+B \rightarrow C$ as thermochemical equation if q is the ...t evolved ; (ii) heat absorbed. State what kind of reactions these are :

(i) .... (......)

(ii) .... (......)

(4) Since all combustion reactions proceed with evolution of heat, they ...... reactions and q is written on the right-hand side with a......sign.

6. (a) Write thermochemical equation for the following reaction :

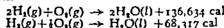
2 moles of hydrogen on burning combine with 1 mole of oxygen to form ...ples of liquid water and liberate 136,634 calories of heat.

(b) Rewrite the above equation to show the formation of 1 instead of 2 ...les of water.

7. Write thermochemical equation for the formation of 1 mole of water ...pour from gaseous hydrogen and oxygen if the heat liberated is 57,798 cal.

8 Fill in the blanks

(a) From either of the equations given below, the heat of combustion of ...drogen is ..... cal.



$$2H_2(g)+O_2(g) \rightarrow 2H_2O(l)+136{,}634 \text{ cal}$$
$$H_2(g)+\tfrac{1}{2}O_2(g) \rightarrow H_2O(l) +68{,}317 \text{ cal}$$

(b) Thermochemical equations can be added or subtracted as if they ...ere algebraic equations From the thermochemical equations for the com...ustion of C (*graphite*) and CO(g).

(i) C (*graphite*)$+O_2(g) \rightarrow CO_2(g)+94{,}052$ kcal

(ii) $CO(g)+\tfrac{1}{2}O_2(g) \rightarrow CO_2(g)+67{,}636$ kcal.

...of the second equation from the first and moving the negative terms ...te side yields

...this manner from the combustion data on experimentally con...ns, one can deduce the heat effects for hard-to-study reactions. ...it is difficult to determine experimentally the heat evolved on ...e to carbon monoxide since some CO might be further oxidized

5. H ... water gas is p... written as :

$H_2O_{(g)}+C$...

or

(*d*) The procedure of combining reactions in order to obtain data on a third reaction depends on the fact that total heat absorbed or evolved in the successive reactions X→Y and Y→Z is the same as in the single direct reaction X→......In other words total heat evolved or absorbed in the reaction X→Z is......(independent of/dependent on) the number of intermediate steps.

(*e*) Heat evolved or absorbed in the reaction X→Z depends only on relative energy contents or heat contents of......and...... It is......of the fact whether the reaction is stepwise or direct.

(*f*) If heat content of Z is greater than that of X, the reaction X→Z is......

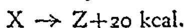
(*g*) The difference between the heat contents of the products and the reactants of the reaction is denoted by $\triangle H$. Mathematically

$\Delta H=$......

In an exothermic reaction $\triangle H$ is......and in an endothermic reaction $\triangle H$ is......

(*h*) Combustion is an......reaction and $\triangle H$ for this reaction is......

(*i*) Instead of writing the heat as a product of reaction with plus or minus sign, modern convention is to write the chemical equation for the reaction and then ΔH for that reaction separately. For example, the equation



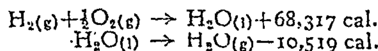
$$X \rightarrow Z+20 \text{ kcal.}$$

should be written as



$$X \rightarrow Z\ ;\ \Delta H=-20 \text{ kcal.}$$

In the same manner, rewrite the following thermochemical equation in the light of the modern convention.



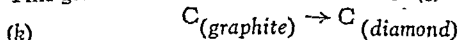
$$H_{2(g)}+\tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}+68{,}317 \text{ cal.}$$
$$H_2O_{(l)} \rightarrow H_2O_{(g)}-10{,}519 \text{ cal.}$$

(*j*) Adding the two equations in the previous item, we get

....

This gives the heat of formation of $H_2O_{(g)}$ as $\triangle H_f=$......

(*k*)



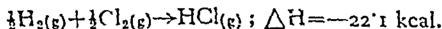
$$C_{(graphite)} \rightarrow C_{(diamond)}$$

is a *hard-to-study* reaction. $\triangle H$ for this reaction can, however, be calculated from the heats of combustion of the two allotropes (=−94,052 and −94,505 cal. per mole respectively) as follows :

....

....

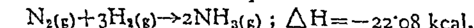
(*l*) The standard heat of formation ($\triangle H^\circ_f$) of a compound is the value of ΔH for the reaction in which 1 mole of that compound is formed from its elements in their commonly occurring state at 25°C. From its equation



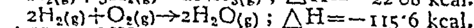
$$\tfrac{1}{2}H_{2(g)}+\tfrac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}\ ;\ \triangle H=-22{\cdot}1 \text{ kcal.}$$

the heat of formation ($\triangle H^\circ_f$) $HCl_{(g)}$ is......kcal. per mole

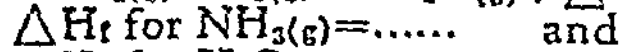
(*m*) From the thermochemical equations



$$N_{2(g)}+3H_{2(g)} \rightarrow 2NH_{3(g)}\ ;\ \triangle H=-22{\cdot}08 \text{ kcal.}$$



$$2H_{2(g)}+O_{2(g)} \rightarrow 2H_2O_{(g)}\ ;\ \triangle H=-115{\cdot}6 \text{ kcal.}$$



$\triangle H_f$ for $NH_{3(g)}$=...... and



$\triangle H_f$ for $H_2O_{(g)}$=......

(*n*) The heat required (or the value of ΔH) in the above case is a measure of the strength of the......holding the atoms together in the molecule and is termed......or......of the molecule.

(*o*) The heat of the dissociation or dissociation energy of HCl is the value of $\triangle H$ for the reaction :

....

(*p*) In the thermochemical equations


$Cl_{2(g)} \rightarrow 2Cl_{(g)}$; $\Delta H + 58{\cdot}0$ kcal.


$HCl_{(g)} \rightarrow H_{(g)} + Cl_{(g)}$; $\Delta H = 103{\cdot}2$ kcal.

ΔH values show that the bond in HCl is .....than the bond in Cl_2.

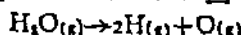
(*q*) In dissociation reactions the heat content of the products is always greater than that of the reactants Hence all dissociation reactions are...... reactions and ΔH for these reactions is always .....

(*r*) From the above it follows that the reverse of dissociation, *i e.*, formation of a chemical bond is on a . .. reaction and ΔH for this is always .....

(*s*) The amount of heat liberated in the formation of a chemical bond is termed bond energy. It is numerically equal to heat of......of the bond.

9. Write thermochemical equation using ΔH for the dissociation of 1 mole of gaseous chlorine into atoms for which the heat required is 58 kcal.

10. Dissociation energies of H_2 and O_2 are 104·2 and 118·3 kcal./mole, respectively and the heat of formation of water (ΔH_f) is $-57{\cdot}8$ kcal. Combine their thermochemical equations to obtain ΔH for the reaction


$$H_2O_{(g)} \rightarrow 2H_{(g)} + O_{(g)}$$

11. From the thermochemical equations

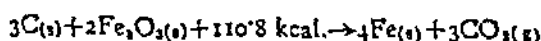

$H_{2(g)} \rightarrow 2H_{(g)}$; $\Delta = 104{\cdot}2$ kcal.


$Cl_{2(g)} \rightarrow 2Cl_{(g)}$; $\Delta = 58{\cdot}0$ kcal.


$HCl_{(g)} \rightarrow H_{(g)} + Cl_{(g)}$; $\Delta = 103{\cdot}2$ kcal.

Calculate the standard heat of formation (ΔH°_f) of $HCl_{(g)}$.

12. Given


$$3C_{(s)} + 2Fe_2O_{3(s)} + 110{\cdot}8 \text{ kcal.} \rightarrow 4Fe_{(s)} + 3CO_{2(g)}$$

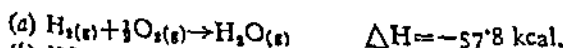
Rewrite the equation using one mole of carbon and use the ΔH notation.

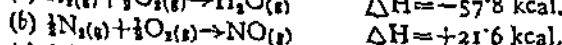
13. Given

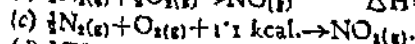

$$\tfrac{1}{2}H_{2(g)} + \tfrac{1}{2}Br_{2(g)} \rightarrow HBr_{(g)} \quad \Delta H = -8{\cdot}60 \text{ kcal./mole HBr}$$

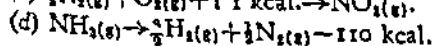
Rewrite the equation for one mole of hydrogen gas and include the heat effect as a term in the equation

14. Which of the following reactions are *exothermic* and which *endothermic* ?


(*a*) $H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H = -57{\cdot}8$ kcal.


(*b*) $\tfrac{1}{2}N_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow NO_{(g)}$ $\Delta H = +21{\cdot}6$ kcal.


(*c*) $\tfrac{1}{2}N_{2(g)} + O_{2(g)} + 1{\cdot}1 \text{ kcal.} \rightarrow NO_{2(g)}$.


(*d*) $NH_{3(g)} \rightarrow \tfrac{3}{2}H_{2(g)} + \tfrac{1}{2}N_{2(g)} - 110$ kcal.

ANSWERS

5. (1) increase, exothermic.
   (2) absorbed, endothermic.
   (3) (i) $A+B \rightarrow C+q$ (exothermic)
   or $A+B \rightarrow C$; $\Delta H = -q$
   (ii) $A+B \rightarrow C-q$ (*endothermic*)
   or $A+B \rightarrow C$; $\Delta H = +q$.
   (4) exothermic, plus.

6. (*a*) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} + 136{,}634$ cal.
   (*b*) $H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} + 68{,}317$ cal.

7. $H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} + 57{,}798$ cal.

8. (*a*) 68,317 cal.

(*b*) $C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} + 26{,}416$ kcal.

(*c*) CO_2

(*d*) Z, independent of

(*e*) X, Z, independent.

(*f*) endothermic.

(*g*) $\Delta H = H_{(products)} - H_{(reactants)}$; negative ; positive.

(*h*) exothermic, negative.

(*i*) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$; $\Delta H - 68{,}317$ cal.
$H_2O_{(l)} \rightarrow H_2O_{(g)}$, $\Delta H = +10{,}519$ cal.

(*j*) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$; $\Delta H - 57{,}798$ cal. ; $\Delta H_f = 57{,}798$ cal.

(*k*) (i) $C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H - 94{,}052$ cal.

(*ii*) $C_{(diamond)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H - 94{,}505$ cal.

Subtracting (ii) from (i) and transferring the negative term t the opposite side,



$C_{(graphite)} \rightarrow C_{(diamond)}$; $\Delta = 453$ cal.

(*l*) $-22·1$ kcal.

(*m*) $-11·04$ kcal. ; 57·8 kcal.

(*n*) bond, heat of dissociation, dissociation energy.

(*o*) $HCl_{(g)} \rightarrow H_{(g)} + Cl_{(g)}$

(*p*) stronger.

(*q*) endothermic positive.

(*r*) exothermic, negative.

(*s*) dissociation.

9. $Cl_{2(g)} \rightarrow 2Cl_{(g)}$; $\Delta H = 58·0$ kcal.

10. (i) $H_{2(g)} \rightarrow 2H_{(g)}$; $\Delta H = 104·2$ kcal.

(ii) $\frac{1}{2}O_{2(g)} \rightarrow O_{(g)}$; $\Delta H = +59·15$ kcal.

(iii) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$; $\Delta H = -57·8$ kcal.

(i)+(ii)−(iii) : $H_2O_{(g)} \rightarrow 2H_{(g)} + O_{(g)}$; $\Delta H = +221·15$ kcal.

11. (i) $\frac{1}{2}H_{2(g)} \rightarrow H_{(g)}$; $\Delta H = 52·1$ kcal.

(ii) $\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)}$; $\Delta H = 29·0$ kcal.

(iii) $HCl_{(g)} \rightarrow H_{(g)} + Cl_{(g)}$; $\Delta H = 103·2$ kcal.

(i)+(ii)−(iii) : $\frac{1}{2}H_2 + \frac{1}{2}Cl_{2(g)} \rightarrow HCl_{(g)}$; $\Delta H = -22·1$ kcal.

12. $C_{(s)} = \frac{2}{3}Fe_2O_{3(g)} \rightarrow \frac{4}{3}Fe_{(s)} + CO_{2(g)}$; $\Delta H = +36·93$ kcal.

13. $H_{2(g)} + Br_{2(l)} \rightarrow 2HBr + 17·2$ kcal.

14. (*a*) is exothermic ; the rest are endothermic.

TYPES OF COLLOIDAL SOLUTIONS

PORCELAIN — SOLID SOL | INK, PAINT — SOL | SMOKE — AEROSOL

CHEESE — GEL | MILK, BUTTER — EMULSION | BISCUIT, CAKE — SOLID FOAM

The Colloidal State

1. **What are Colloids?**—In 1802, a Scottish chemist, Thomas Graham (18[illegible]–18[illegible]) made a distinction between solutes [illegible] ly. [illegible] ize [illegible] ue) [illegible] is now known to be very indefinite as crystalloids can be obtained in a colloidal dispersion and *vice versa*, depending upon conditions. So now we speak of colloidal state instead of colloids.

2. *Colloidal Dispersions.*—At present the main distinction between colloidal solutions and true solutions is one of particle [illegible] than molecules but smaller [illegible] arious particles are given [illegible], 1mμ = 10^{-7} cm.)

Coarse dispersions	*Fine dispersions*	*Colloidal dispersions*	*True solutions*
More than 50,000 mμ	100 to 50,000 mμ	1 to 100 mμ	0·2 to 1 mμ

In the case of colloidal dispersions the substance in solution is termed the *dispersed phase* while the *medium in which the* particles are dispersed is called the *dispersion medium*. Various types of colloidal dispersions are:

TYPE	NAME	EXAMPLES
1. Solid in a solid	Solid sol.	Procelain; coloured glass; alloys.
2. Solid in a liquid	Sol.	Indian ink; paints, white of an egg.
3. Solid in a gas	Aerosol	Smoke; volcanic dust
4. Liquid in a solid	Gel	Cheese; jellies
5. Liquid in a liquid	Emulsion	[illegible]
6. Liquid in a gas	Aerosol	[illegible]
7. Gas in a solid	Sold foam	[illegible]
8. Gas in a liquid	Foam	[illegible]

Suspensions are heterogeneous and their particles settle dow on standing. Because of the smaller particle size colloidal solution appear homogeneous to the naked eye although they are found defi nitely heterogeneous when looked under a microscope. Particles o a colloidal solution do not settle down on standing and cannot b separated by ordinary filtration. This can, however, be filtere through special filter papers with fine pores and made to settle b centrifiugation.

Colloidal state may thus be defined as heterogeneous disper sion of two immiscible phases (which are more or less permanent) and possessing certain characteristic properties.

3. Preparation of Colloidal Solutions.

(*a*) **Preparation of Lyophilic Solutions.** Certain substances like gum-arabic, glue, starch and gelatin, readily pass into colloidal solution on warming with suitable liquids. These are known as **Intrinsic colloids** and the colloidal solutions obtained from them are referred to as **Lyophilic sols.** Colloidal solution of intrinsic colloids in water are termed **hydrophilic sols.**

(*b*) **Preparation of Lyophobic Sols.** Substances which do not pass into colloidal solution like the intrinsic colloids are called **Extrinsic Colloids.** Special methods are employed for preparation of colloidal solutions of the extrinsic colloids. These are referred to as **Lyophobic sols.** Colloidal solutions of extrinsic colloids in water are termed **Hydrophobic sols.**

Since the colloidal state depends on the particle size, there are two general ways in which colloidal solutions of extrinsic colloids can be obtained. They are :

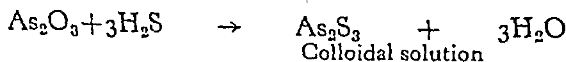
(*a*) **Condensation**—*increasing the size of smaller particles up to the colloidal size.*

(*b*) **Dispersion**—*breaking of the bigger particles (of fine or coarse suspencion) down to the colloidal size.*

Different methods employed for the purpose are given below :

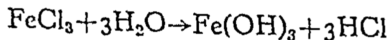
(A) CONDENSATION METHODS

(*i*) **By Chemical Reaction.** On passing hydrogen sulphide through a dilute solution of arsenious oxide in water, arsenious sulphide is precipitated in a colloidal form.



$$As_2O_3 + 3H_2S \rightarrow \underset{\text{Colloidal solution}}{As_2S_3} + 3H_2O$$

(*ii*) **By Hydrolysis.** A colloidal solution of ferric hydroxide is obtained by boiling dilute solution of ferric chloride when hydrolysis occurs.



$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

(*iii*) **Reduction.** Gold is obtained in a colloidal form by reducing a solution of gold chloride with formaldehyde or tannic acid.

(*iv*) **By Oxidation.** Sulphur is precipitated in a colloidal form when hydrogen sulphide is bubbled through an oxidising agent (bromine water, nitric acid).



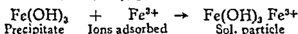
$$Br_2 + H_2S \rightarrow \underset{\text{Colloidal}}{S} + 2HBr$$

(B) DISPERSION METHODS

(*i*) **By Grinding.** Coarser particles are broken to the colloidal size by grinding in a colloid mill. A *protective colloid* is often added to stabilise the colloidal suspension obtained. For example, in the preparation of *aquadag* (a graphite lubricant) tannin is used to stabilise the suspension. Similarly gum-arabic is used to stabilise the suspension of lampblack in water (Indian ink).

(*ii*) **Peptization.** On adding a small quantity of ferric chloride solution to a freshly precipitated and well-washed ferric hydroxide precipitate, it passes into a colloidal solution.

This process of passing of a precipitate into colloidal solution on adding an electrolyte is called **peptization.** It involves the adsorption of suitable ions from the electrolyte by the fine particles of the precipitate and they form the colloidal solution. For example, Fe^{3+} are adsorbed by $Fe(OH)_3$ particles in the ferric hydroxide sol.



$$\underset{\text{Precipitate}}{Fe(OH)_3} + \underset{\text{Ions adsorbed}}{Fe^{3+}} \rightarrow \underset{\text{Sol. particle}}{Fe(OH)_3\,Fe^{3+}}$$

The electrolyte added is termed a **dispersing agent or peptizing agent.**

(*iii*) **Bredig's method.** Colloidal solution of gold, silver and other metals are frequently prepared by striking an electric arc beneath the surface of a liquid containing some protective colloid to prevent coalescing (precipitation). Tiny particles are torn from wires by the arc to form a colloidal suspension. The liquid is kept cool by surrounding the trough with ice.

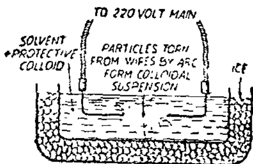


Fig 27·1—Bredig's method by electro-dispersion.

(*iv*) **Emulsification.** Oil and water yield a lasting emulsion when agitated in the presence of soap (*emulsifying agent*).

4. Properties of Colloidal Solutions.

(1) **Non-Settling.** *Colloidal* solutions are heterogeneous in character and the suspended *particles remain* suspended indefinitely. Some large colloidal particles may settle but very slowly.

(2) **Tyndall effect.** If a strong beam of light is passed through a colloidal solution, it becomes visible as it spreads out. *This is due to diffusion of light by colloidal particles*—**Tyndall effect.**

(3) **Brownian movement.** Colloidal particles are found to be in a continual motion in zig-zag path when seen under an ultra-microscope. This motion is called the Brownian movement.

Dust particles floating in air in a dark room constitute a colloidal solution. When a beam of light is passed through the dark room, the "dancing of dust particles in the beam of light which becomes visible" are examples of Brownian movement and Tyndall effect, respectively.

(4) **Adsorption.** Colloidal solutions are known for tremendous adsorption power. This is due to large surface area of colloidal particles. Use of colloidal charcoal in gas masks is based on its capacity for adsorption of poison gases.

(5) **Electrical charge.** Colloidal particles are electrically charged, e.g., colloidal arsenic sulphide is negatively charged while colloidal ferric hydroxide is positively charged. In an electric field, the colloidal particles move towards an oppositely charged electrode —**Electrophoresis** or **Cataphoresis.**

Expt. 1 Cover the end of a *U*-tube *A* with a parchment paper. Fill it with a colloidal solution of arsenic trisulphide through the opening at the bottom and cork. Now invert *A* and slip over its end two wide glass tubes, *B*, *B* with rubber bands (Fig. 27·2) Put dilute acetic acid in *B*, *B*, insert platinum wires in them and pass electric current from the mains. Colloidal particles are seen migrating towards the anode (+) leaving a part of the liquid clear near the cathode (−).

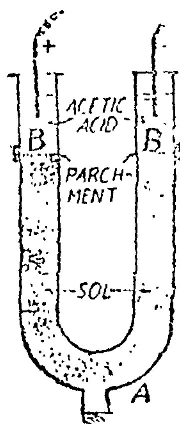


Fig. 27·2—Electrophoresis.

(6) **Coagulation.** The colloidal particles are coagulated or precipitated by adding oppositely charged ions or even heating in some cases. For example, arsenic sulphide sol is coagulated by adding sodium chloride (Na^+), better by Ba^{2+} in barium chloride and most easily by Al^{3+} in aluminium chloride. White of an egg is coagulated just by warming.

(7) **Dialysis.** Colloidal particles are retained by porous membrane, e.g., parchment bag, while crystalloids pass through. This colloidal solution can be purified by enclosing it in a parchment bag and placing in a running water. Crystalloids present as impurity pass out through the parchment membrane leaving pure sol behind. The process of purification is called **Dialysis** and the apparatus used is called a **Dialyser** (Fig. 27·3).

The process of diffusion is accelerated to some extent by using hot water in place of cold water (**Hot dialysis**) or by dipping

positive and negative electrodes in the water surrounding the parchment bag (Electrodialysis) as shown in Fig. 27·4.

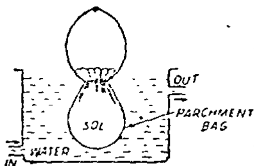


Fig. 27·3—Dialysis.

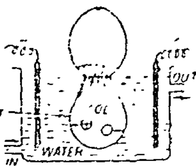


Fig. 27·4—Electrodialysis.

5. **Practical Applications of Colloids.**

(1) Fertile soils are colloidal in nature.

(2) River water is a colloidal suspension of clay in water. This is coagulated by salt water in the sea with the formation of deltas.

(3) Sensitive emulsion deposited on photographic plates, films and papers is colloidal in nature.

(4) Dyeing is essentially an adsorption phenomenon by colloidal particles of the mordant frequently used.

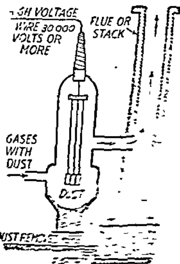
(5) Skins are colloidal in nature and tanning of leather involves swelling and subsequent precipitation of their colloidal particles.

(6) Manufacture of soap involves colloidal changes. Cleansing action of soap is explained on the basis that soap solution is colloidal in nature. It emulsifies greases and adsorbs the dirt particles and thus washes them away.

(7) Colloidal medicines have proved to be more effective as they are easily absorbed by the system.

(8) Nuisance of smoke in big industrial areas is removed by precipitation of smoke (colloidal solution of carbon particles in air) in a Cottrell precipitator shown in Fig. 27·5

(9) The purification of water [illegible]



(10) Inks, paints, rubber, cement, plaster, synthetic plastics and graphite lubricants are all colloidal solutions.

(11) Clarification of sugar juice [illegible] colouring matter by colloidal charcoal.

QUESTIONS

Essay-type Questions

1. What are colloids ? Discuss some of their characteristic properties.
(Punjab Pre-Medical/Pre-Engg./B.Sc. I Year 1962)

2. Explain the term 'Colloid's.
Discuss some of the important methods for the preparation of Colloids.
(Delhi Pre-Medical 1972)

3. Distinguish between Colloidal solution and True solution.

4. Write short note on "Dialysis". *(Delhi H.S. 1968)*

5. What are the characteristics of a "Colloidal solution" ?
In what respects does a colloidal solution differ from a true solution ?
Mention one example of a colloidal substance interfering in the qualitative detection of cations and explain how this difficulty can be overcome.

Test Your Understanding

6. Fill in the blanks in the following :

(*i*) Colloidal particles are......than molecules but......than the visible grains.

(*ii*) A colloidal solution of solid in solid is termed......, that of solid in liquid is termed......while that of solid in gas is called......

(*iii*) Cheese, milk and cloud are examples of......,......and......respectively.

(*iv*) Glue and gelatin which readily pass into colloidal solution are examples of......colloids and the colloidal solutions obtained from them are termed......

(*v*) Process of passing of a precipitate into colloidal solution on adding an electrolyte is called......while the electrolyte added is terms......

(*vi*) Movement of colloidal particles in an electrical field towards...... electrodes, is called......or......

(*vii*) Diffusion of light by colloidal particles is termed......

(*viii*) Continual motion of colloidal particles in zig-zag paths is called......

KEY

(*i*) bigger, smaller ; (*ii*) solid sol, sol, aerosol ; (*iii*) gel, emulsion, aerosol ; (*iv*) intrinsic, lyophilic sols ; (*v*) peptization, peptizing agent ; (*vi*) oppositely charged, electrophoresis, cataphoresis ; (*vii*) Tyndall effect ; (*viii*) Brownian movement.

Appendix

NEW TYPE TEST PAPER I

(Based on Chapters 1 to 27)

Completion Test

1. Fill in the blanks with the correct word or words in the following statements :

(*a*) A homogeneous mixture of a solid and a liquid is called a......

(*b*) The substance which dissolves is termed ...... and the substance in which it dissolves is called ......

(*c*) The water present in the crystals is called ......

(*d*) In the process of distillation......and......go side by side.

(*e*) Sublimation is the conversion of ..into...on heating and reverse on cooling.

True-False Test

2. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements :

(*a*) A solute may usually be separated from the solvent by *filtration*.

(*b*) Solubility generally *increases* with the rise of temperature.

(*c*) Sedimentation removes *dissolved* matter.

(*d*) Camphor may be purified by *sublimation*.

(*e*) The crystals have *regular geometrical shapes*.

(*f*) Crystals are deposited from an *unsaturated* solution.

(*g*) A precipitate can be separated by *sublimation*.

Matching Test

3. Mark each item in list II with appropriate [illegible] (ii), (iii), etc., so that [illegible] items in list I. One of [illegible]

List I		List II
(i) Chemical balance	(iii)	Measurement of temperature.
(ii) Burette, pipette and graduated cylinder	(..)	Measurement of weight.
(iii) Themometer	(...)	Settling of insoluble substance from a liquid.
(iv) Barometer	(...)	Saparation of insoluble Substance from a liquid.
(v) Sedimentation	(...)	Measurement of volume.
(vi) Distillation	(...)	Formation of insoluble substance on mixing two liquids.
(vii) Filtration	(...)	Purification of liquids.
(viii) Precipitation	(...)	Measurement of pressure.

Completion Test

4. Fill in the blanks with the correct word or words in the following elements :

(*i*) Anything which occupies space and has weight is called...

(*ii*) Solids have definite......and definite......

(*iii*) An atom is the smallest particle of......which can take part in......

(*iv*) Molecule is the smallest particle of...... It can be sub-divided but (loses/retains)......its characteristic properties on sub-division.

(*v*) A permanent change in which the identity of a substance changes is called a......

(*vi*) Groups of atoms reacting as single atoms are known as...

(*vii*) Valency is the number of......or......atoms or double the number of......atoms that an atom or a radical can hold in a compound.

(*viii*) A chemical equation represents a......with the help of symbols and formulae.

(*ix*) The percentage of sodium and chlorine in three specimens of sodium chloride prepared by different methods was found to be the same. This illustrates the Law of......

(*x*) An element *A* combines with another element *B* to form two compounds in which 1 gm. and 1·5 gm. of *B* separately combine with *x* grams of *A*. This illustrates the Law of......

(*xi*) The nucleus of an atom is made up of......and......

(*xii*) Atoms of the same element possessing different weights are called......

5. Fill in the blanks with the correct word or words in the following statements :

(*i*) Boyle [illegible] states that......remaining [illegible] constant, the...... of a given quan[illegible] gas is inversely propor[illegible] to its......

(*ii*) Char[illegible] w states that......remaining [illegible] constant, the...... of a given quant[illegible] f a gas is......to its absolute temperature.

(*iii*) The n[illegible]ber of molecules contained in one gram molecule of a gas is called......

(*iv*) *W* gram of an element, when treated with excess of dilute acid liberated *V* c.c. of hydrogen at N.T.P. Its equivalent weight=......

(*v*) W_1 grams of the oxide were obtained from W_2 grams of a metal. The equivalent weight of the metal is......

(*vi*) W_1 grams of a metal gave W_2 grams of its chloride. The equivalent weight of the metal is......

(*vii*) The atomic weight divided by equivalent weight is equal to......

(*viii*) The products of......and......of a solid element is approximately equal to 6·4.

6. Fill in the blanks with the correct word or words in the following statements :

(*i*) Conditions which favour a chemical reaction are......., ..., ..., ...and......

(*ii*) An unbalanced equation is against the law of......

(*iii*) In a chemical equation reactants as well as the products must be represented as......

(*iv*) Chemical equations representing the quantity of heat evolved or absorbed during the chemical reaction are called...... equations.

(*v*) Reactions which are favoured by light are called......

(*vi*) The two parts constituting a molecule are separately called......

7. Fill in the blanks with the correct word or words in the following statements :

(*i*) Avogadro's law states that equal......of all gases under similar conditions of......and......contain equal number of......

(*ii*) Molecular weight=......× Vapour density.

(*iii*) The number of molecules present in one gram molecule of a gas is called......and is equal to......

(*iv*) Equivalent weight of a substance is its number of parts by weight which combine with or displace directly or indirectly...... parts by weight of hydrogen or......parts by weight of oxygen or ......parts by weight of chlorine.

(*v*) The weights of various ions liberated by passing the same current through different electrolytes are in the ratio of their......

(*vi*) By dividing the percentage of different elements in a molecule by the corresponding atomic weight, we get. ....

Selection Test

8. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) Washing soda is (*a*) a mixture, (*b*) a compound, (*c*) an element.

(*ii*) Two liquids having widely different boiling points can be separated by (*a*) Evaporation, (*b*) Distillation, (*c*) Sublimation.

(*iii*) Sulphur and iron filings react when (*a*) brought in close contact, (*b*) heated, (*c*) exposed to sunlight.

(*iv*) Burning of charcoal is a (*a*) physical change, (*b*) endothermic reaction, (*c*) exothermic reaction.

(*v*) Symbol of copper is (*a*) Co, (*b*) Cu, (*c*) C.

(*vi*) The symbolic expression for a molecule is called (*a*) sy bol, (*b*) formula, (*c*) equation.

(*vii*) Ammonium (NH_4) is a (*a*) Simple radical, (*b*) Ac radical, (*c*) Compound radical.

(*viii*) Valency of ferrous radical is (*a*) 2, (*b*) 3, (*c*) 4.

(*ix*) Atomic number of an element is equal to the number (*a*) protons, (*b*) neutrons, (*c*) sum of protons and neutrons.

(*x*) Covalent linkage is set up by (*a*) lending, (*b*) borrowin (*c*) lending and borrowing, (*d*) mutual sharing of electrons.

(*xi*) The formula of zinc sulphate is (*a*) Zn_2SO_4, (*b*) Zn (*c*) $ZnSO_3$, (*d*) $ZnSO_4$.

(*xii*) Gases react in simple ratio by (*a*) volumes, (*b*) atom (*c*) weights.

True-False Test

9. In the following statements mark T before true stat ments and F before false ones. Supply the word or words whic must be substituted for the italicised words in the false statement

(*i*) *Gases* have definite volume but no shape.

(*ii*) *Elements* cannot be decomposed into simpler substance

(*iii*) Ingredients of a *mixture* may be present in any ratio.

(*iv*) A *compound* can be separated into its constituents b simple mechanical means.

(*v*) Energy is either evolved or absorbed in the formation c a *chemical compound.*

(*vi*) A *chemical change* results in the formation of a substanc with entirely different properties.

(*vii*) A chemical equation *expresses* the relative weights of th reactants and products.

(*viii*) A chemical equation *does not express* the relative volume of the gaseous reactants and products.

(*ix*) In a chemical reaction the molecules *do not undergo an change.*

(*x*) *Electrons* are particles of negligible mass and carry on unit negative charge.

10. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements.

(i) The pressure of a gas *increases* with the rise of temperature.

(ii) The rates of diffusion of gases are *inversely proportional* to their densities.

(iii) The gas equation is $P_1V_1T_1 = P_2V_2T_2$.

(iv) Equal *number of molecules* of all gases occupy *equal volumes* under similar conditions of temperature and pressure.

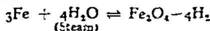
(v) Molecular weight of a substance is the relative weight of its molecule as compared with the *weight of an atom of carbon* (C^{12}-isotope) taken as 12 *amu*.

(vi) The molecular weight of a *non-volatile* substance can be found out by the Victor Meyer's method.

(vii) Atomic weight is the ratio between the average weight of an atom of the element and *one-twelfth part* of the weight of an atom of carbon.

(viii) Empirical formula gives the *simplest whole number ratio between* the atoms of different elements present in the molecule of a substance.

(ix) The reaction



$$3Fe + \underset{(Steam)}{4H_2O} \rightleftharpoons Fe_3O_4 + 4H_2$$

will proceed to completion if hydrogen is allowed to escape.

(x) If the concentration of the reactants is increased, the rate of reaction will *also increase*.

Matching Test

11. Mark each item in list II with appropriate numbers—(i), (ii), (iii), etc.—so that it becomes related with the corresponding items in list I.

List I	List II
(i) Tyndall Effect	(.) Exchange of acid and basic radicals between two compounds.
(ii) Brownian movement	(..) Reactions in which heat is evolved.
(iii) Double decomposition	(..) Change in the rate of a Chemical reaction.
(iv) Decomposition	(..) Reactions in which heat is absorbed.
(v) Endothermic reactions	(...) Continuous motion of colloidal particles.

List I	List II
(*vi*) Catalysis	(...) Reactions favoured by light.
(*vii*) Exothermic reaction	(...) Diffusion of light by colloidal particles.
(*viii*) Isobars	(...) Breaking down of a co plex substance into simp ones.
(*ix*) Photochemical reaction	(...) Different elements hav same atomic weight.

12. Mark each item in list II with appropriate numbers—(*ii*), (*iii*), etc.—so that it becomes related with the correspond item in list I.

(*i*) Graham	(...) Vapour density method determining molecular w ght.
(*ii*) Vapour density	(...) Law of partial pressures
(*iii*) Molecular weight	(...) Equal volumes of all ga under similar conditions temperature and press contain equal number atoms.
(*iv*) Regnault	(...) Number of gram molecu per unit volume.
(*v*) Dalton	(...) Ratio between the wei of 1 molecule of a gas a the weight of 1 atom hydrogen.
(*vi*) Berzelius	(...) Law of Diffusion.
(*vii*) Avogadro	(...) Equal volumes of all ga under similar conditions temperature and press contain equal number molecules.
(*viii*) Dulong and Petit	(...) Ratio between the wei of 1 mol. of a gas and weight of 1 mol. of drogen.
(*ix*) Active mass	(...) Determination of ator weight.

Multiple Choice Test

13. In the following statements put √ mark on the m suitable word or expression out of the various possible alternati suggested therein :

(*i*) The gram molecular weight of a gas occupies at N.T a volume of (*a*) one c.c., (*b*) one litre, (*c*) 22·4 litres.

(ii) Avogadro's number is the number of molecules present in (a) one c.c., (b) one litre, (c) one gram, (d) one gram molecular weight of the gas.

(iii) The pressure P exerted by two gases, having partial pressures p_1 and p_2 and enclosed in a space will be equal to (a) p_1+p_2, (b) $\frac{p_1+p_2}{2}$, (c) $\sqrt{p_1 \times p_2}$

(iv) If t_1 and t_2 be the time taken for diffusion of V c.c. of the gases A and B, d_1 and d_2 their densities, M_1 and M_2 their molecular weights and r_1 and r_2 their rates of diffusion, then,

$$\frac{t_1}{t_2}=(a)\quad \sqrt{\frac{d_1}{d_2}},\ (b)\quad \sqrt{\frac{M_2}{M_1}},\ (c)\quad \frac{r_2}{r_1}.$$

(v) The atomic weight of an element is (a) weight of one atom of it; (b) weight of one atom of it compared with that of carbon atom; (c) twelve times the ratio between the weight of one atom of it and the weight of one atom of carbon.

(vi) In the reaction :



$$N_2+3H_2 \rightleftharpoons 2NH_3-22{,}400\ cal.$$

the yield of ammonia will increase if (1) temperature is (a) increased, (b) decreased, (c) kept at 1000°C ; (2) pressure is (a) increased, (b) decreased, (c) kept at atmospheric pressure.

Completion Test

14. Fill in the blanks with correct word or words in the following statements :

(a) The splitting up of a molecule into ions in solution is called.....

(b) The process of decomposition of an electrolyte in solution by electric current is called.....

(c) When a copper ion changes to copper atom, it (gains/loses).....(one/two/three).....electrons.

(d) Bases in aqueous solution form no negative ions other than .....ions.

(e) Neutralisation is the reaction between ... and ...... resulting in the formation of ... and ... .

(f) The basic nature of sodium carbonate solution is due to its.....

(g) A normal solution contains ... of the solute dissolved per litre.

(h) Normality is the ratio between ... and ... of the solute.

(i) The molecular weight of an acid divided by its basicity is equal to its.....

(j) The acidity of a base can be obtained by dividing its ..... by its.....

List I	List II
(*vi*) Catalysis	(...) Reactions favoured by light.
(*vii*) Exothermic reaction	(...) Diffusion of light by colloidal particles.
(*viii*) Isobars	(...) Breaking down of a complex substance into simpler ones.
(*ix*) Photochemical reaction	(...) Different elements havin same atomic weight.

12. Mark each item in list II with appropriate numbers—(*i*) (*ii*), (*iii*), *etc.—so that it becomes related* with the correspondin item in list I.

(*i*) Graham	(...) Vapour density method fo determining molecular weight.
(*ii*) Vapour density	(...) Law of partial pressures.
(*iii*) Molecular weight	(...) Equal volumes of all gase under similar conditions o *temperature and pressur* contain equal number o atoms.
(*iv*) Regnault	(...) Number of gram *molecule* per unit volume.
(*v*) Dalton	(...) Ratio between the weigh of 1 molecule of a gas an the weight of 1 atom o hydrogen.
(*vi*) Berzelius	(...) Law of Diffusion.
(*vii*) Avogadro	(...) Equal volumes of all gase under similar conditions o temperature and pressur contain equal number o molecules.
(*viii*) Dulong and Petit	(...) Ratio between the weigh *of 1 mol. of a gas and th* weight of 1 mol. of hy drogen.
(*ix*) Active mass	(...) Determination of atomi weight.

Multiple Choice Test

13. In the following statements put √ mark on the mos suitable word or expression out of the various possible alternative suggested therein :

(*i*) The gram molecular weight of a gas occupies at N.T.I a volume of (*a*) one c.c., (*b*) one litre, (*c*) 22·4 litres.

(*ii*) Avogadro's number is the number of molecules present in (*a*) one c.c., (*b*) one litre, (*c*) one gram, (*d*) one gram molecular weight of the gas.

(*iii*) The pressure P exerted by two gases, having partial pressures p_1 and p_2 and enclosed in a space will be equal to (*a*) p_1+p_2, (*b*) $\frac{p_1+p_2}{2}$, (*c*) $\sqrt{p_1 \times p_2}$.

(*iv*) If t_1 and t_2 be the time taken for diffusion of V c.c. of the gases *A* and *B*, d_1 and d_2 their densities, M_1 and M_2 their molecular weights and r_1 and r_2 their rates of diffusion, then,

$$\frac{t_1}{t_2} = (a) \quad \sqrt{\frac{d_1}{d_2}}, \ (b) \ \sqrt{\frac{M_2}{M_1}}, \ (c) \ \frac{r_1}{r_2}.$$

(*v*) The atomic weight of an element is (*a*) weight of one atom of it ; (*b*) weight of one atom of it compared with that of carbon atom ; (*c*) twelve times the ratio between the weight of one atom of it and the weight of one atom of carbon.

(*vi*) In the reaction :



$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22{,}400 \text{ cal.}$$

the yield of ammonia will increase if (1) temperature is (*a*) increased, (*b*) decreased, (*c*) kept at 1000°C ; (2) pressure is (*a*) increased, (*b*) decreased, (*c*) kept at atmospheric pressure.

Completion Test

14. Fill in the blanks with correct word or words in the following statements :

(*a*) The splitting up of a molecule into ions in solution is called......

(*b*) The process of decomposition of an electrolyte in solution by electric current is called......

(*c*) When a copper ion changes to copper atom, it (gains/loses)......(one/two/three)......electrons.

(*d*) Bases in aqueous solution form no negative ions other than......ions.

(*e*) Neutralization is the reaction between.. .. and......... resulting in the formation of..... and. ..

(*f*) The basic nature of sodium carbonate solution is due to its

(*g*) A normal solution contains......of the solute dissolved per litre.

(*h*) Normality is the ratio between and. ....of the solute.

(*i*) The molecular weight of an acid divided by its basicity is equal to its ..

(*j*) The acidity of a base can be obtained by dividing its...... by its... ..

List I	List II
(*vi*) Catalysis	(...) Reactions favoured by light.
(*vii*) Exothermic reaction	(...) Diffusion of light by colloidal particles.
(*viii*) Isobars	(...) Breaking down of a complex substance into simpler ones.
(*ix*) Photochemical reaction	(...) Different elements having same atomic weight.

12. Mark each item in list II with appropriate numbers—(*i*), (*ii*), (*iii*), etc.—so that it becomes related with the corresponding item in list I.

(*i*) Graham	(...) Vapour density method for determining molecular weight.
(*ii*) Vapour density	(...) Law of partial pressures.
(*iii*) Molecular weight	(...) Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of atoms.
(*iv*) Regnault	(...) Number of gram molecules per unit volume.
(*v*) Dalton	(...) Ratio between the weight of 1 molecule of a gas and the weight of 1 atom of hydrogen.
(*vi*) Berzelius	(...) Law of Diffusion.
(*vii*) Avogadro	(...) Equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.
(*viii*) Dulong and Petit	(...) Ratio between the weight of 1 mol. of a gas and the weight of 1 mol. of hydrogen.
(*ix*) Active mass	(...) Determination of atomic weight.

Multiple Choice Test

13. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) The gram molecular weight of a gas occupies at N.T.P. a volume of (*a*) one c.c., (*b*) one litre, (*c*) 22·4 litres.

(ii) Avogadro's number is the number of molecules present in (a) one c.c., (b) one litre, (c) one gram, (d) one gram molecular weight of the gas.

(iii) The pressure P exerted by two gases, having partial pressures p_1 and p_2 and enclosed in a space will be equal to (a) p_1+p_2, (b) $\frac{p_1+p_2}{2}$, (c) $\sqrt{p_1 \times p_2}$.

(iv) If t_1 and t_2 be the time taken for diffusion of V c.c. of the gases A and B, d_1 and d_2 their densities, M_1 and M_2 their molecular weights and r_1 and r_2 their rates of diffusion, then,

$$\frac{t_1}{t_2} = (a) \quad \sqrt{\frac{d_1}{d_2}}, \quad (b) \quad \sqrt{\frac{M_2}{M_1}}, \quad (c) \quad \frac{r_1}{r_2}.$$

(v) The atomic weight of an element is (a) weight of one atom of it; (b) weight of one atom of it compared with that of carbon atom; (c) twelve times the ratio between the weight of one atom of it and the weight of one atom of carbon.

(vi) In the reaction :



$$N_2+3H_2 \rightleftharpoons 2NH_3+22{,}400 \text{ cal.}$$

the yield of ammonia will increase if (1) temperature is (a) increased, (b) decreased, (c) kept at 1000°C; (2) pressure is (a) increased, (b) decreased, (c) kept at atmospheric pressure.

Completion Test

14. Fill in the blanks with correct word or words in the following statements :

(a) The splitting up of a molecule into ions in solution is called......

(b) The process of decomposition of an electrolyte in solution by electric current is called.. ...

(c) When a copper ion changes to copper atom, it (gains/loses) .....(one/two/three)......electrons.

(d) Bases in aqueous solution form no negative ions other than......ions.

(e) Neutralization is the reaction between .. ...and.. . resulting in the formation of..... and. ....

(f) The basic nature of sodium carbonate solution is due to its......

(g) A normal solution contains . of the solute dissolved per litre.

(h) Normality is the ratio between . . and .. . of the solute.

(i) The molecular weight of an acid divided by its basicity is equal to its......

(j) The acidity of a base can be obtained by dividing its by its......

15. Fill in the blanks with correct word or words in the following statements :

(*i*) Substances which in water solution conduct electric current are called......

(*ii*) On passing electric current through fused sodium chloride, sodium is liberated at the......while chlorine is collected at the.....

(*iii*) Acids are substances which produce no......ions other thar ......ions in solution.

(*iv*) Copper sulphate solution is......towards litmus due to.....

(*v*) The basicity of......is the number of replaceable.....presen in its molecule.

16. Fill in the blanks to make the following statements com plete and correct :

(*i*) The latest standard of atomic weight is......as......

(*ii*) The equivalent weight of oxygen is...... ; atomic weigh is...... ; and molecular weight is......

(*iii*) Oxidation is.........of electrons and reduction is.........o electrons.

(*iv*) Potassium ferrocyanide is a......salt, while ferrous am monium sulphate is a......salt.

(*v*) The number of electrons present in the outermost shell o all halogens is......and that of all alkali metals is......

(*vi*) On heating mercuric chloride......

Selection Test

17. In the following statements put √ mark on the mos suitable word or expression out of the various possible alternative suggested therein :

(*a*) The nitrate ion is electrically (*i*) positively charged, (*ii* negatively charged, (*iii*) neutral.

(*b*) A strong electrolyte (*i*) is ionized almost completely, (*ii* does not ionize, (*iii*) produces few ions in solution.

(*c*) Chloroform does not give any precipitate with silve nitrate because (*i*) the precipitate of silver chloride is soluble i chloroform, (*ii*) it is an organic substance, (*iii*) it is a nor electrolyte.

(*d*) When the same quantity of electricity passes throug solution of different electrolytes, the weights of different ion liberated at the electrodes are in the ratio of their (*i*) atomi weights, (*ii*) equivalent weights, (*iii*) concentration in gram per litre.

(*e*) Sulphuric acid is a strong acid because it is (*i*) highl ionized, (*ii*) an oxy-acid, (*iii*) an electrolyte.

(*f*) Solution of copper sulphate is acidic due to (*i*) hydrolysis (*ii*) ionization, (*iii*) presence of sulphate ion, (*iv*) presence of Cu^{2+}

(*g*) Substances react in the ratio of their (*i*) equivalent weights, (*ii*) degree of ionization, (*iii*) normalities, (*iv*) molecular weights.

True-False Test

18. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements :

(*i*) *Sodium ions* react with water to give hydrogen.

(*ii*) A state of *dynamic equilibrium* exists between un-ionized molecules and ions.

(*iii*) Sodium chloride gives white precipitate of silver chloride with silver nitrate due to the presence of *chlorine in its molecule.*

(*iv*) The weight of an ion liberated during electrolysis is proportional to *the quantity of electricity passed.*

(*v*) Acid salts contain *some replaceable hydrogen.*

(*vi*) Water is *necessarily formed* in the process of neutralization.

(*vii*) Acids *do not change* the colour of phenolphthalein.

19. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements :

(*i*) The degree of ionization depends on *temperature.*

(*ii*) The electrolytes ionize when *electric current is passed through their aqueous solutions.*

(*iii*) In electroplating a bright and smooth deposit is obtained *at low temperature and high current density.*

(*iv*) The aqueous solution of a *salt* contains a positive ion other than H^+ and a negative ion other than OH^-.

(*v*) A *base* reacts with sulphur trioxide to give a sulphate.

Multiple Choice Test

20. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) During electrolysis of sodium chloride solution, the substance liberated at the anode is (*a*) sodium, (*b*) hydrogen, (*c*) chlorine.

(*ii*) Strength of an acid depends upon (*a*) the number of hydrogen atoms in its molecule, (*b*) its concentration, (*c*) its degree of ionization.

(*iii*) Conductivity of a solution is proportional to (*a*) the dilution, (*b*) volume of solution, (*c*) strength of electric current.

(*iv*) The quantity of solute dissolved per litre in a sub-normal solution is (*a*) equal to, (*b*) more than, (*c*) less than its gram equivalent weight.

(*v*) Complex salts (*a*) contain two cations, (*b*) contain two anions, (*b*) do not ionize, (*d*) give complex ions in solution.

21. Which of the following statements are correct and which are incorrect ? Give one reason in each case in support of your answer.

(*i*) A solution of sodium carbonate has no action on litmus paper.

(*ii*) Atomic weight is the basis of the modren periodic classification of elements.

(*iii*) Ions do not carry any electric charge.

(*iv*) A solution of copper sulphate has no action on litmus paper.

(*v*) A solution of ferric sulphate in water has no action on litmus paper.

(*vi*) Ions are the same as atoms.

(*Delhi H.S. 1971, 70*)

22. Rewrite the following statements in a correct and complete form and name the law on which each of these statements is based.

(*a*) If enough oxygen and sulphur dioxide are put into a balloon to give respectively pressures of 0·5 and 0·7 atmospheres, the total pressure will be 1·2 atmospheres.

(*b*) The rate of diffusion of helium in four times the rate of diffusion of sulphur dioxide. (He=4 ; S=32)

(*c*) If 1·12 litres of O_2 contain 3×10^{22} molecules at N.T.P., 0·56 litres of SO_2 will also contain 3×10^{22} molecules.

(*d*) For oxygen, the product of its volume and pressure, *pv*, will have constant value.

(*Delhi H.S. 1969*)

23. Correct the mistake, if any, in the following statements.

(*i*) Eq. wt. of an acid=Mol. wt. × acidity.

(*ii*) Chemically similar elements are placed in the same period of the periodic table.

(*iii*) Hydrolysis is the ionisation of a salt on dissolving in water.

(*iv*) Gram molecular weight of a substance is the weight of its molecules in grams. (*Delhi H.S. 1969*)

24. Correct the following statements giving appropriate reasons in not more than two lines :—

(*a*) Conversion of water into steam is a chemical change.

(*b*) A molecule of hydrogen contains one atom.

(*c*) Covalent compounds are ionised in solution.

(*d*) Potassium chlorate is a strong reducing agent.

(*e*) Equivalent weight of a compound is twice its vapour density.

(*f*) Atomic weight is the basis of modern Periodic classification. (*Delhi H.S. 1972*)

KEY TO THE SOLUTIONS

1. (*a*) Solution, (*b*) Solute ; solvent, (*c*) Water of crystallization, (*d*) Evaporation ; condensation, (*e*) Solid ; vapour.

2. (*a*) F, distillation, (*b*) T, (*c*) F, suspended, (*d*) T, (*e*) T, (*f*) F, saturated, (*g*) F, filtration.

3. (*iii*), (*i*), (*v*), (*vii*), (*ii*), (*viii*), (*vi*), (*iv*).

4. (*i*) Matter, (*ii*) shape, volume, (*iii*) an element, chemical reactions, (*iv*) a substance, loses, (*v*) chemical change, (*vi*) radicals, (*vii*) hydrogen, chlorine, oxygen, (*viii*) chemical reaction, (*ix*) definite proportions, (*x*) multiple proportions, (*xi*) protons, neutrons, (*xii*) isotopes.

5. (*i*) Temperature ; volume ; pressure, (*ii*) pressure ; volume ; directly proportional, (*iii*) Avogadro's number, (*iv*) $\frac{W}{V} \times 11{,}200$, (*v*) $\frac{W_2}{W_1 - W_2} \times 8$, (*vi*) $\frac{W_1}{W_2 - W_1} \times 35.5$, (*vii*) valency, (*viii*) at. wt. ; sp. heat.

6. (*i*) Contact ; Solution ; Heat ; Light ; Electricity ; Percussion ; Catalysis, (*ii*) Conservation of Mass, (*iii*) molecules, (*iv*) Thermo-chemical, (*v*) Photo-chemical, (*vi*) Radicals.

7. (*i*) Volumes ; temperature ; pressure ; molecules, (*ii*) 2. (*iii*) Avogadro's number ; 6.023×10^{23}, (*iv*) 1·008 ; 8 ; 35·5, (*v*) Equivalent weights. (*vi*) Relative number of atoms.

8. (*i*) (*b*), (*ii*) (*b*), (*iii*) (*b*), (*iv*) (*c*), (*v*) (*b*), (*vi*) (*b*), (*vii*) (*c*), (*viii*) (*a*), (*ix*) [illegible]

9. (*i*) F [illegible]

(*vi*) T ; (*vii*) T [illegible]

of atoms resulting in the formation of new molecules ; (*x*) T.

10. (*i*) T, (*ii*) F, inversely proportional to the square root of their densities, (*iii*) F, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$, (*iv*) T, (*v*) T, (*vi*) F, volatile, (*vii*) T, (*viii*) T, (*ix*) T, (*x*) T.

11. (*iii*), (*vii*), (*vi*), (*v*), (*ii*), (*ix*), (*i*), (*iv*) (*viii*).

12. (*iv*), (*v*), (*vi*), (*ix*), (*iii*), (*i*), (*vii*), (*ii*), (*viii*).

13. (*i*) (*c*), (*ii*) (*d*), (*iii*) (*a*), (*iv*) (*a*), (*v*) (*c*), (*vi*) (1) (*b*) ; (2) (*a*).

14. (*a*) Ionization, (*b*) electrolysis, (*c*) gains, two, (*d*) hydroxyl, (*e*) acid, base, salt, water, (*f*) hydrolysis, (*g*) One gram equivalent weight, (*h*) grams per litre, equivalent weight, (*i*) equivalent weight, (*j*) molecular weight, equivalent weight.

15. (*i*) electrolytes, (*ii*) cathode ; anode, (*iii*) positive ; hydrogen, (*iv*) acidic, hydrolysis, (*v*) an acid, hydrolysis, (*vi*) an acid hydrogen atoms.

16. (*i*) Weight of carbon (C^{12} isotope) taken, 12 am (*ii*) 8, 16, 32 ; (*iii*) Loss, Gain ; (*iv*) Complex, Double ; (*v*) 7, (*vi*) Sublimes.

17. (*a*)—(*ii*) ; (*b*)—(*i*) ; (*c*)—(*iii*) ; (*d*)—(*ii*) ; (*e*)—(*i*) ; (*f*) (*i*) ; (*g*)—(*i*).

18. (*i*) F—Sodium atoms ; (*ii*) T ; (*iii*) F—Chloride ic which it gives on ionization ; (*iv*) T ; (*v*) T ; (*vi*) T ; (*vii*) T.

19. (*i*) T ; (*ii*) F—they are dissolved in water ; (*iii*) (*iv*) T ; (*v*) T.

20. (i)–(*c*) ; (ii)—(*c*) ; (iii)–(*a*) ; (iv)—(*c*) ; (v)—(*d*).

21. All are incorrect. Give reasons.

22. (*a*) Dalton's law of partial pressures—see its definition correcting the statement.

(*b*) Graham's law of gasoues diffusion.

(*c*) 1.5×10^{22} molecules ; Avogadro's law.

(*d*) For a given quantity of oxygen at constant tempertu the product.. ...... ; Boyle's law.

23. (*i*) Eq. wt. of an acid=Mol. wt.÷acidity.

(*ii*) Write 'group' in place of 'period'.

(*iii*) Hydrolysis in the reaction between salt and water give the parent acid and base.

(*iv*) Gram molecular weight of a substance is its wei in grams numerically equal to molecular weight.

24. (*a*) Conversion of water into steam is a physical chai since the change is temporary and identity of the compound (H does not change.

(*b*) A molecule of hydrogen contains two atoms shown its Cp/Cv ratio=1·4.

(*c*) Covalent compounds are not ionised in solution si covalent bond is not an ionic bond.

(*d*) Potassium chlorate is a strong oxidising agent since, it a tendency to lose oxygen and give potassium chloride.

(*e*) Molecular weight of a compound is twice its vap density as deduced by the application of Avogadro's law.

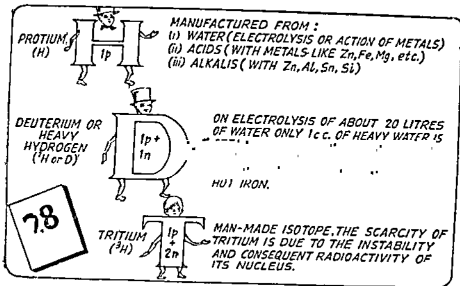
(*f*) Atomic number is thebasis of modern periodic classif tion since according to modern periodic law—the propertie elements are a periodic function of their atomic numbers.

PART II

INORGANIC CHEMISTRY

(Descriptive Chemistry of Elements—Non-metals and Metals and their Compounds in the light of Modern Physical Concepts)

"Let us fix the word element precisely now and for the future, as meaning a substance with definite chemical and spectroscopic properties which may or may not be a mixt[ure of] isotopes"



Hydrogen

1. H... was known early in the sixteenth ... btained by the action of sulphuric ... ever, first recognised as a definite substance in 1766 by an English scientist, Henry Cavendish, who studied its properties and called it "inflammable air". He also showed in 1781 that water is the only product of combustion of hydrogen in air. Lavoisier in 1783 suggested the present name hydrogen (Greek: *hydro*=water, *genus*=I produce).

2. Occurrence.—Free or elementary hydrogen is present in air only in traces, probably derived from volcanic gases. Hydrogen is present in the atmosphere of the sun.

In the combined state, hydrogen is very widely distributed. It is an essential constituent of all acids and alkalis while one-ninth of water by weight is h...



Henry Cavendish
(1731—1810)
English physicist and chemist; he discovered properties of hydrogen in 1766 and identified ... ent.

... animal tissues

3. **Preparation of hydrogen.**—Water, acids, and alkalis constitute the chief sources from which hydrogen is prepared. Different methods employed are:

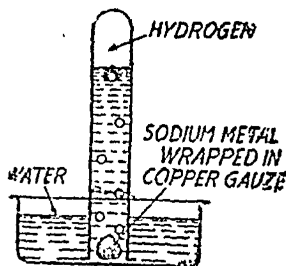
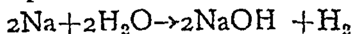


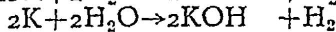
Fig. 28·1—Sodium reacts with water.

(1) **From Water.** Decomposition of water, in order to prepare hydrogen, may be effected in a number of ways.

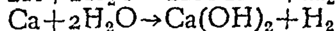
(*a*) **By the action of metals.** (*i*) AT ROOM TEMPERATURE. Certain metals, *e.g.*, sodium, potassium and calcium, are so active that they can decompose water at the room temperature.



$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$



$$2K + 2H_2O \rightarrow 2KOH + H_2$$



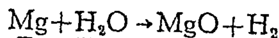
$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$$

Action is quite violent in the case of sodium and more so with potassium (hydrogen evolved catches fire). In the case of calcium the reaction is fairly slow and unlike sodium and potassium it is heavier than water. Sodium amalgam can be used with advantage in place of the metal.

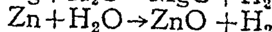
Expt. 1. Wrap a small piece of sodium in a copper gauze. Place it in a trough of water and invert a test tube over the metal piece (Fig. 28·1). Bubbles of hydrogen are evolved in a rapid stream and collect in the test tube. Add a drop of phenophthalein to the water in the trough, it turns pink.

Certain other less active metals decompose water only when used in the form of couples, *e.g.*, Zinc-copper couple, Aluminium-mercury couple. The couples are important reducing agents, due to the nascent hydrogen which they liberate from water. Zinc copper couple is prepared by immersing granulated zinc in dilute copper sulphate solution and washing the product free from adhering salts.

(*ii*) AT BOILING POINT. Magnesium powder, zinc powder and aluminium powder break up boiling water giving hydrogen and oxide of the metal.

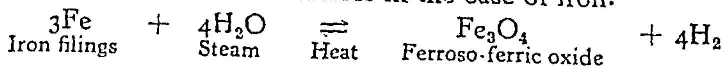


$$Mg + H_2O \rightarrow MgO + H_2$$



$$Zn + H_2O \rightarrow ZnO + H_2$$

(*iii*) BY PASSING STEAM OVER HEATED METALS. Heated magnesium, zinc, cobalt, nickel, lead and tin react with water in the form of steam. The reaction is reversible in the case of iron.

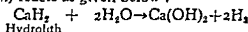


$$\underset{\text{Iron filings}}{3Fe} + \underset{\text{Steam}}{4H_2O} \underset{\text{Heat}}{\rightleftharpoons} \underset{\text{Ferroso-ferric oxide}}{Fe_3O_4} + 4H_2$$

Expt 2. Heat iron filings in a hard glass tube and pass a current of steam over it. Test the gas collecting in the gas jar over water. It is found to be hydrogen.

(*b*) **By Electrolysis.** Water is made a conductor by adding some dilute acid or alkali to it. On passing electric current, hydrogen is liberated at the cathode while oxygen is collected at the anode.

(c) By the action of Hydrides. Metallic hydrides can decompose water at ordinary temperature. For example, calcium hydride (*hydrolith*) reacts as given below :

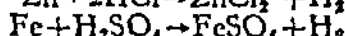


$$\underset{\text{Hydrolith}}{CaH_2} + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

(d) [illegible] ...als, *e.g.*, zinc, iron [illegible] and hydrochloric [illegible] Aluminium and tin [illegible] ...gnesium gives the purest product but is most expensive.



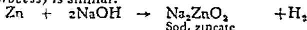
$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$



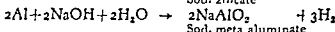
$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

(e) [illegible]

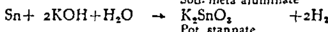
and iron (*Silicol process*) is similar.



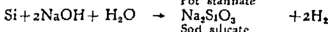
$$Zn + 2NaOH \rightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2$$



$$2Al + 2NaOH + 2H_2O \rightarrow \underset{\text{Sod. meta aluminate}}{2NaAlO_2} + 3H_2$$

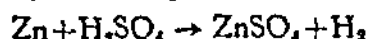


$$Sn + 2KOH + H_2O \rightarrow \underset{\text{Pot stannate}}{K_2SnO_3} + 2H_2$$



$$Si + 2NaOH + H_2O \rightarrow \underset{\text{Sod silicate}}{Na_2SiO_3} + 2H_2$$

4. **Preparation in the Laboratory.**—Fig. 28·2 shows the type of apparatus commonly used in the laboratory preparation of hydrogen by the action of dilute sulphuric or hydrochloric acid on granulated zinc.



$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

The gas is collected over water. As hydrogen forms an explosive mixture with air, the apparatus should be air-tight and no flame should be brought near it.

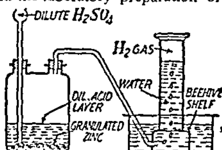


Fig. 28·2—Laboratory preparation of hydrogen

Hydrogen so prepared from zinc and sulphuric acid is always contaminated with a number of impurities. Various impurities present and their removal is given below :

Impurities	Removal
(i) O_2 (from air).	Removed by passing over heated copper.
(ii) SO_2, CO_2 and oxides of nitrogen.	Removed by passing the gas through strong caustic potash solution.
(iii) H_2S, PH_3 and AsH_3.	By passing through strong potassium permanganate solution and finally through silver nitrate solution to remove traces of AsH_3
(iv) Moisture.	By drying over $CaCl_2$ or P_4O_{10}.

Hydrogen is usually prepared in the laboratory in a Kipp's automatic generator (Fig. 28·3). It consists of bulb *A* with a long stem *F* fitting into the neck of the *base* made of two bulbs *B* and *E*. The metal is placed in the glass bulb B and the acid is poured into *A* until *E* is full and the granulated zinc in *B* is covered with acid Reaction occurs with the liberation of hydrogen gas and continues till the pressure of the gas accumulated pushes the acid out of *B* into *E* and on to *A* through *F* and the level in *B* falls to *L*. The reaction ceases now as the metal and acid are no longer in contact.

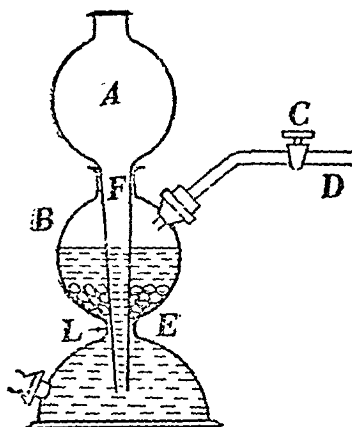


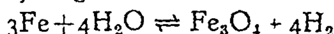
Fig. 28·3—Kipp's apparatus.

Whenever gas is needed, it is taken out through *D* by opening the tap *C*. The gas having escaped, the pressure in the middle bulb *B* falls. Sulphuric acid again rises into this bulb to produce more gas. The reaction continues till the gas again pushes the acid out of the bulb *E*.

5. **Manufacture of Hydrogen.**—Large quantities of hydrogen are needed in industry for different purposes. It is mostly prepared from water. Various methods used for its manufacture are

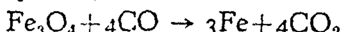
(1) **By Electrolysis of Water.** Wherever electricity is cheap, electrolysis of water is the cheapest method for the manufacture of hydrogen. Water is made conductor by addition of a little acid or an alkali (20% caustic soda) and the electric current is passed when hydrogen is collected at the cathode. Oxygen evolved at anode is collected as a *by-product*. The type of cell used is shown in Fig. 28·4. The asbestos diaphragm is a porous diaphragm used to prevent the mixing of hydrogen and oxygen.

(2) **Lane's Process.** By passing alternate currents of steam and water gas over red hot iron. When steam is passed for about 10 minutes (*oxidation period*) iron gets converted into its magnetic oxide and hydrogen is collected.

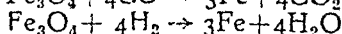


$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

The magnetic oxide is then reduced back to spongy iron when water gas ($CO + H_2$) is blown over heated oxide for 20 minutes (*reduction period*).

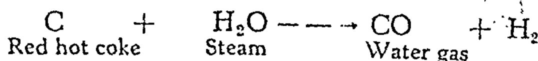


$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$



$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

(3) **From Water Gas.** When steam is blown over red hot carbon, a mixture of carbon monoxide and hydrogen called water gas is obtained.



$$\underset{\text{Red hot coke}}{C} + \underset{\text{Steam}}{H_2O} \longrightarrow \underset{\text{Water gas}}{CO + H_2}$$

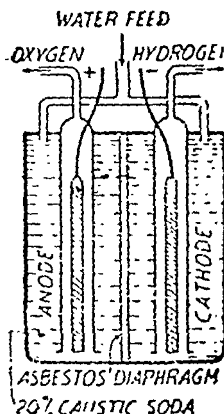
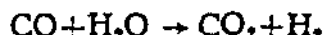


Fig. 28·4—Manufacture of hydrogen by electrolysis of water

Hydrogen can be manufactured from water gas by removing carbon monoxide in two different ways :

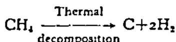
(*a*) *By liquefaction*. Water gas is cooled under pressure when carbon monoxide condenses and hydrogen is left behind.

(*b*) *Through its replacement by hydrogen* (Bosch Process). For this purpose water gas is mixed with twice its volume of steam and passed over a heated catalyst, usually oxide of iron mixed with [illegible] Carbon monoxide which can be [illegible] ater under pressure and an equal [illegible]

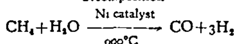


$$CO + H_2O \rightarrow CO_2 + H_2$$

(4) **From Natural Gas.** Natural gas is mainly methane. Methane can be converted into hydrogen by thermal decomposition or by mixing it with steam and passing the mixture over a nickel catalyst heated to 900°C.



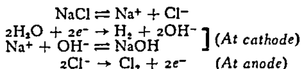
$$CH_4 \xrightarrow[\text{decomposition}]{\text{Thermal}} C + 2H_2$$



$$CH_4 + H_2O \xrightarrow[900^\circ C]{\text{Ni catalyst}} CO + 3H_2$$

Carbon monoxide and hydrogen are separated as already described under Bosch process.

(5) **As By-product.** Large quantities of hydrogen are obtained as by-product during the manufacture of caustic soda by electrolysis of sodium chloride and the manufacture of sodium by electrolysis of fused caustic soda.



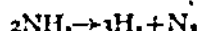
$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$\left.\begin{array}{l} 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ Na^+ + OH^- \rightleftharpoons NaOH \end{array}\right] \textit{(At cathode)}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad \textit{(At anode)}$$

Transportation of Hydrogen Cheap transportation of hydrogen has :n an important commercial problem for many years As it cannot be [illegible]

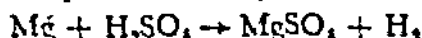
[illegible] itination ammenia is cracked by passing it over heated catalysts yielding a xture of hydrogen (75%) and nitrogen (25%)



$$2NH_3 \rightarrow 3H_2 + N_2$$

Nitrogen is not separated from the mixture which is used as it is, for rposes such as welding and brazing, sintering of powdered metals, manufac- e of nylon, etc.

6. **Pure Hydrogen.**—A sample of pure hydrogen can be pre- ired by the action of pure dilute sulphuric acid on magnesium.



$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

It can, however, be obtained in the purest form by the electrolysis of a warm solution of barium hydroxide in U-tube using nickel electrodes (Fig. 28'5). The hydrogen evolved is passed over heated platinum gauze when any oxygen present react with hydrogen to form water. The gas is dried by passing through caustic potash sticks and P_4O_{10}. Hydrogen is finally adsorbed in palladium and the impurities not adsorbed are pumped out. Pure hydrogen is regenerated by heating palladium foil *under reduced pressure.*

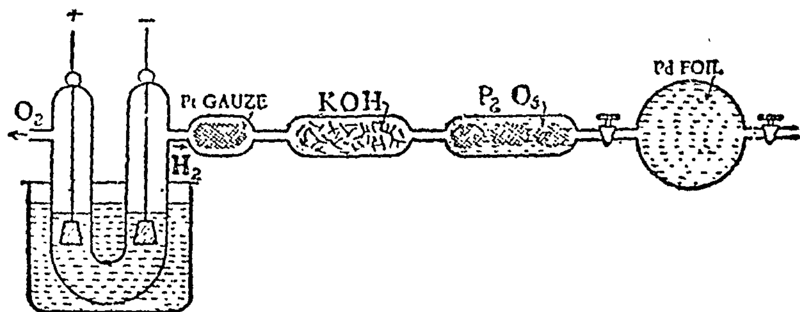


Fig. 28'5—Preparation of pure hydrogen.

7. **Physical Properties of Hydrogen.**—(*i*) It is colourless, odourless and tasteless gas, less soluble in water than oxygen.

(*ii*) It is the lightest gas known. One litre of hydrogen at N.T.P. weighs only 0'09 gram. Its lightness is demonstrated by experiments as given below :

Expt. 1. Invert a cylinder full of air over another full of hydrogen. Test the gas in the upper cylinder, it is found to be hydrogen. Hydrogen being lighter collects in the upper cylinder.

Expt. 2. Fill a toy balloon with hydrogen and leave it in air. It is found to rise up and up till it collapses due to escape of hydrogen by diffusion.

Expt. 3. Bubble hydrogen gas through a soap solution. Bubbles are obtained full of hydrogen gas. These are found to rise up higher and higher till they burst Hydrogen, present in them, can be lighted by bringing a candle flame near them.

(*iii*) James Dewar (1898) succeeded in liquefying the gas cooling under high pressure. Liquid hydrogen (b.p. −253°C) can be solidified by evaporating to an ice-like solid (m.p. −259°C).

(*iv*) An interesting property of the gas is its adsorption or occlusion by certain metals, *e.g.*, platinum and palladium.

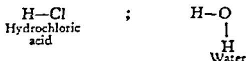
Adsorption *is a process of soaking up only on the surface in contrast to* **absorption** *which is a process of soaking up through the entire mass.*

8. **Chemical Properties of Hydrogen.**—Hydrogen shows four important types of combination :

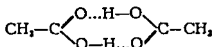
(*i*) Electrovalency in forming hydrogen ion, H^+ which is hydrated in water as the hydronium or hydroxonium ion, H_3O^+. The relative activity of aqueous solutions depends on the hydrogen ion concentration.

(*ii*) Electrovalency in forming the hydride ion, H^- as in NaH, CaH_2, etc.

(iii) Covalency as in hydrochloric acid, water, etc.



(*iv*) Hydrogen bonding as in the molecule H_2F_2 represented as H—F...H—F or H_3F_3 (H—F...H—F...H—F). Hydrogen bond is shown by a dotted line. Dimerised molecule of acetic acid is written as:



Chemical properties of hydrogen discussed below are related to these modes of chemical combination.

(*i*) **Action of Litmus.** Hydrogen is neutral to litmus.

(*ii*) **Combustion.** Hydrogen is a combustible gas and it burns in air or oxygen with nearly invisible pale blue flame. Water is the only product of combustion when hydrogen burns. This can be demonstrated by a simple experiment illustrated in Fig. 28·6.

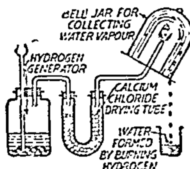


Fig. 28·6—Water is the only product when hydrogen burns.

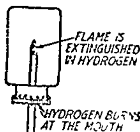


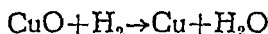
Fig. 28·7—Hydrogen is combustible but not a supporter of combustion.

It is a combustible gas but not a supporter of combustion.

Expt. 4. Fill a bottle with hydrogen and hol[illegible] mouth downwards. Introduce a burning splinter of wood [illegible]. The gas is found to burn at the mouth of the bottle wh[illegible] is extinguished (Fig. 28·7).

(iii) **Reducing Property.** When hydrogen gas is passed over heated metallic oxides, it removes the oxygen from them and unites with it to form water. *The process of removal of oxygen from a compound is termed* **reduction** *and substances like hydrogen which bring about reduction are called* **reducing agents**.

Expt. 5. Fit up the apparatus as shown in Fig. 28'8. Heat some black oxide of copper in the pyrex tube and pass a current of dry hydrogen over it. Metallic copper reddish in colour is obtained.



$$CuO+H_2 \rightarrow Cu+H_2O$$

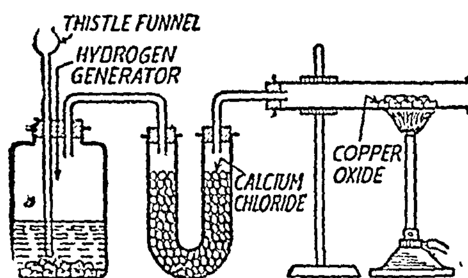


Fig. 28'8—Reduction of copper oxide to metallic copper by hydrogen.

(iv) **Combination with Elements.** Hydrogen is not a very active element and does not combine with other elements very readily. Under suitable conditions, however, it can be made to unite with other elements. For example,

(a) *With oxygen* it combines *on burning* to give water.

(b) *With chlorine* it combines *when exposed to sunlight* to give hydrochloric acid.

(c) *With bromine* it combines *on heating* while *with iodine* it combines *when heated in presence of a catalyst.*

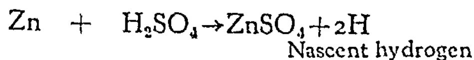
(d) *With nitrogen* it combines *under pressure and in the presence of catalyst.*

(e) *With metals* like sodium or potassium it gives hydrides which are not so stable as hydrides of non-metals.

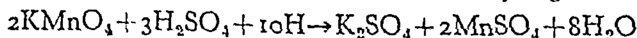
(v) **Hydrogenation.** When hydrogen is bubbled through liquids oils in the presence of finely divided nickel, these are converted into solid fats. This is hydrogenation of oils used in the manufacture of *vanaspati ghee.*

(vi) **Nascent Hydrogen.** If hydrogen gas is bubbled through acidified potassium permanganate, colour is not discharged. To the same if we add some zinc pieces, tiny bubbles of hydrogen are found to rise and potassium permanganate is decolorised.

Hydrogen, produced *in situ,* in the second case is more active and called *Nascent hydrogen (nearly born).* It is atomic hydrogen while ordinary hydrogen is in the form of molecules.

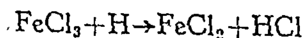


$$Zn + H_2SO_4 \rightarrow ZnSO_4 + \underset{\text{Nascent hydrogen}}{2H}$$



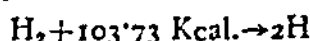
$$2KMnO_4+3H_2SO_4+10H \rightarrow K_2SO_4+2MnSO_4+8H_2O$$

Ferric chloride solution (*yellow*) is decolorised by adding zinc pieces and hydrochloric acid. This is also due to reduction of ferric chloride to ferrous chloride (*faint green solution*) by nascent hydrogen.



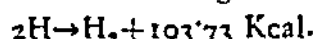
$$FeCl_3+H \rightarrow FeCl_2+HCl$$

(vii) Atomic Hydrogen. When hydrogen is passed through an electric arc, it dissociates into atoms. The endothermic reaction is written as follows :



$$H_2 + 103{\cdot}73 \text{ Kcal.} \rightarrow 2H$$

The heat stored up is liberated when hydrogen atoms strike a solid surface and recombine to give molecules.



$$2H \rightarrow H_2 + 103{\cdot}73 \text{ Kcal.}$$

This was used by Langmuir in atomic hydrogen torch (Fig. 28·9).

(viii) Active Hydrogen. When silent electric discharges are passed through hydrogen at room temperature and very low pressure, active hydrogen is produced. Active hydrogen readily combines with lead and sulphur to produce their hydrides. It reduces cupric and ferric salts at ordinary temperature.

[illegible] (1) Due to its low density, hydro- [illegible] gas bags for airships. On account [illegible] tendency to leak, it is replaced by helium with 93% as much "lifting power" as hydrogen

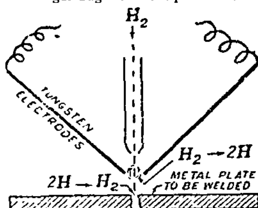


Fig. 28·9—Atomic hydrogen torch.

(2) *As a fuel* hydrogen is an important gaseous fuel. Fuel gases, *e.g.*, coal gas, water gas, oil gas contain hydrogen as an important constituent. It is used in oxy-hydrogen torch (Fig. 28·10) used for welding purposes. It is also used in the atomic hydrogen torch.

(3) It is used *in the manufacture of hydrogen compounds.* For example :

(*a*) *Ammonia.* This is manufactured by the direct union of nitrogen and hydrogen (Haber's process) and is used in the manufacture of fertilizers, nitric acid and explosives.

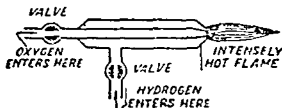
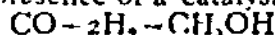


Fig. 28·10—Oxy hydrogen torch.

(*b*) *Methanol.* It is obtained from hydrogen and carbon monoxide reacting in the presence of a catalyst.



$$CO + 2H_2 \rightarrow CH_3OH$$

(*c*) *Petrol substitutes.* Gasoline is obtained by hydrogenation of high boiling fractions of crude petroleum or a paste of powdered coal in crude oil under pressure and in the presence of a catalyst. Mixture of lower hydrocarbons obtained is called synthetic petrol.

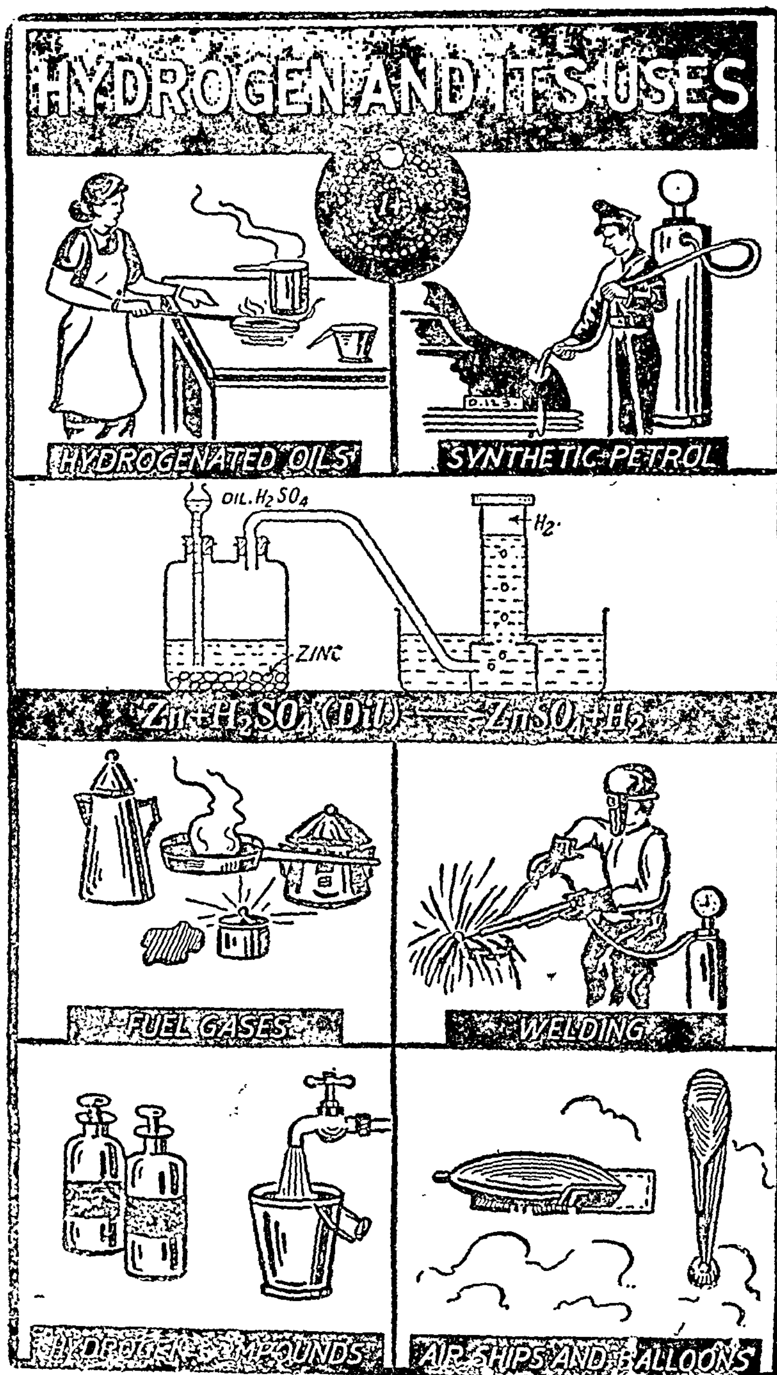

HYDROGEN AND ITS USES
HYDROGENATED OILS
SYNTHETIC PETROL
DIL. H_2SO_4
H_2
ZINC
$Zn + H_2SO_4\ (Dil) \longrightarrow ZnSO_4 + H_2$
FUEL GASES
WELDING
AIR SHIPS AND BALLOONS

Fig. 28·11.

(4) *For hydrogenation of oils* in the presence of finely divided nickel as catalyst. Oils get hardened as a result of hydrogenation and are used under the name *vanspati ghee* and in edible fats.

(5) For providing reducing atmosphere in furnaces.

10. **Tests for Hydrogen.**—Hydrogen burns with a nearly colourless flame producing nothing but water. This serves as a test for the gas.

11. **Isotopes of Hydrogen.**- ... are given on page 1·82. Ordinary

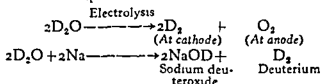
presented by the wt.=3) has been

Their relative abundance in nature is as follows :

H . D . T . : 5000 : 1 : 10^{-17}

The scarcity of tritium is due to the instability and consequent radioactivity of its nucleus.

On electrolysis of water, the higher isotope of hydrogen is evolved first. The small residue of water left is richer in the heavier isotope and is called *heavy water* or deuterium oxide (D_2O). On electrolysis of about 20 litres of water only 1 c.c. of heavy water is obtained. Deuterium is obtained by electrolysis of heavy water or its decomposition with sodium or red hot iron.



$$2D_2O \xrightarrow{\text{Electrolysis}} \underset{(At\ cathode)}{2D_2} + \underset{(At\ anode)}{O_2}$$

$$2D_2O + 2Na \longrightarrow \underset{\text{Sodium deuteroxide}}{2NaOD} + \underset{\text{Deuterium}}{D_2}$$

Properties of Deuterium. Properties of deuterium are similar to those of protium. For example, it is colourless, odourless and tasteless. It is insoluble in water and bad conductor of heat. Its atomicity is 2. Some other physical constants are :

Property	Protium	Deuterium
B.P. (°A)	20·38	23·59
M.P. (°A)	13·95	18·65
Latent heat of fusion cal./mol.	28·0	52·2

In general properties of isotopes are qualitatively very similar but there is quantitative difference especially when the percentage difference in mass is appreciable. *Property differences due to differences in mass are called* isotope effects.

In chemical reactions protium and deuterium show quantita- ... For example, ionization of ... heavy water. Rate of breaking of H—H bonds is 18 times the rate of breaking of D—D bonds. Similarly rate of reaction between H_2 and Cl_2 is 13·4 times the rate of reaction between D_2 and Cl_2.

For elements heavier than hydrogen the isotope effect is mu smaller because the percentage difference in mass is very sma For example, $_{53}I^{127}$ reacts only 1·02 times faster than $_{53}I^{129}$ and tl properties are nearly the same.

During electrolysis of water H—O bonds break faster tha D—O bonds and we get only protium in the beginning leavir heavier water behind.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Cold water+(*i*) Sodium, (*ii*) Potassium, (*iii*) Calcium, and (*iv*) C cium hydride.

2. *Boiling water*+Magnesium, Zinc *or* Aluminium powder.

3. Steam+(*i*) Iron, and (*ii*) Red hot coke.

4. Dil. hydrochloric, or sulphuric acid+(*i*) Zinc, (*ii*) Magnesium, a (*iii*) Iron.

5. Sodium hydroxide+(*i*) Zinc, (*ii*) Aluminium, (*iii*) Tin, and (*iv*) S con.

6. Nascent hydrogen+(*i*) Acidified potassium permanganate, and Ferric chloride.

QUESTIONS

Essay-type Questions

1. (*a*) Give one method (except electrolysis) for the preparation hydrogen from each of the following : (*a*) water, (*b*) dilute sulphuric acid, (*c*) caustic soda solution.

(*b*) What is nascent hydrogen and how is it formed ? Give examples two such chemical reactions in which nascent hydrogen takes part. Show nascent hydrogen is more active than ordinary hydrogen.
(*Punjab H.S. 1961 ; Punjab Pre-Univ. 1*

2. Give a method for the large-scale preparation of hydrogen. How pure hydrogen obtained ? What is nascent hydrogen and how is it forme Describe giving equations and the conditions under which hydrogen reacts (*i*) chlorine, (*ii*) nitrogen, and (*iii*) carbon. (*All-India H.S. 1*

3. Describe one method for the manufacture of hydrogen. Give name and formula of the chief hydrogen compound of each of the follow elements : (*a*) Oxygen, (*b*) Nitrogen, (*c*) Chlorine, and (*d*) Sulphur. State bri the *conditions* under which it reacts with : (*a*) nitrogen, (*b*) chlorine, and (*c*) bon. How would you distinguish between hydrogen and carbon monoxide
(*Punjab Pre-Univ. 1*

4. Give reasons for the following :

(*a*) Ferric chloride is reduced when zinc and sulphuric acid are adde its solution and *not by passing hydrogen through it.*

(*b*) Concentrated sulphuric acid and pure zinc are not used for preparation of hydrogen in the laboratory. (*Rajasthan Inter. 1*

5. Write a short note on Heavy hydrogen. (*Delhi H.S. 1966,*

6. Write a short note on Isotope effects.

Test Your Understanding

7. Tick the correct answer in the following :

Hydrogen CANNOT be obtained.

(i) From water gas, (ii) by electrolysis of water, (iii) by the action of steam on ferroso-ferric oxide (Fe_3O_4), (iv) by the action of concentrated alkali on aluminium, (v) by the action of dilute hydrochloric acid on zinc.

8. Fill in the blanks in the following :

(i) Hydrogen is manufactured in the.. ...process by passing alternate currents of steam and water gas over ......

(ii) In the..... process carbon monoxide of water gas is replaced by ....

(iii) Hydrogen is used in the synthesis of ......, ...and......

(iv) Ordinary lighter isotope of hydrogen is termed .....

(v) Property differences due to differences in mass of isotopes are called .....

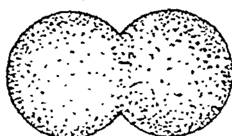
KEY

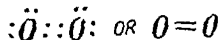
7. (iii).

8. (i) Lane's, red hot iron ; (iii) Bosch, hydrogen ; (iii) ammonia, methanol, synthetic petrol ; (iv) protium ; (v) isotope effects.

29

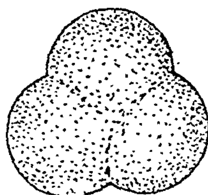
OXYGEN

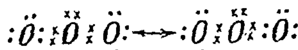




MANUFACTURED BY,
(i) ELECTROLYSIS OF WATER
(ii) FRACTIONAL EVAPORATION OF LIQUID AIR

OZONE





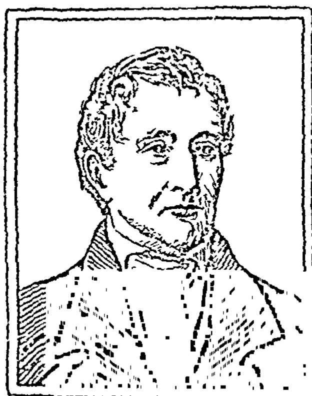


PREPARED BY PASSING SILENT ELECTRIC DISCHARGES THROUGH OXYGEN OR AIR

Oxygen and Ozone

OXYGEN

1. **Historical.**—The Chinese observed, as early as the eighth century, that air consists of two chief ingredients, one of which supported combustion while the other did not. Priestley and Scheele prepared oxygen within a few months of each other by heating suitable oxygen compounds. For example, Scheele prepared by focussing sun's rays on mercuric oxide (Fig. 29·1). However, it remained for the French chemist Lavoisier to carrry on further experiments and explain correctly the part oxygen plays in so many reactions.



Karl Whilhlem Scheele
(1742—86)
Swedish chemist whose experiments on air and combustion led to his discovery of oxygen (1772). His results were published late in 1777.



Joseph Priestley
(1733—1804)
English chemist who discovered oxygen in 1774. He also recognised the production of oxygen by green plants in sunlight.

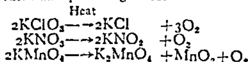
2. **Occurrence.**—About one-fifth of the atmosphere in which we live is *free or elementary oxygen.* In the combined state it is present in water (89% by weight), earth's crust (about 5%), plants and animal tissue (50—70%). In fact combined oxygen is muchs more plentiful than free oxygen.



Fig. 29·1—Scheel's experiment.

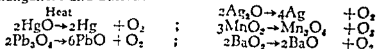
3. **Preparation.**—Several methods employed for the preparation of oxygen are :

(1) *By heating certain oxygen containing salts, e.g.,* chlorates, nitrates and permanganates.



$$2KClO_3 \xrightarrow{Heat} 2KCl + 3O_2$$
$$2KNO_3 \longrightarrow 2KNO_2 + O_2$$
$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

(2) *By heating metallic oxides, e.g.,* those of mercury, lead, silver, manganese and barium.



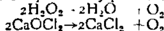
$$2HgO \xrightarrow{Heat} 2Hg + O_2 \quad ; \quad 2Ag_2O \rightarrow 4Ag + O_2$$
$$2Pb_3O_4 \rightarrow 6PbO + O_2 \quad ; \quad 3MnO_2 \rightarrow Mn_3O_4 + O_2$$
$$2BaO_2 \rightarrow 2BaO + O_2$$

(3) *By the action of sodium peroxide on water.*



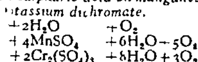
$$2N_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

(4) *By the decomposition of peroxide or hypochlorites.*



$$2H_2O_2 \rightarrow 2H_2O + O_2$$
$$\underset{\text{Bleaching powder}}{2CaOCl_2} \rightarrow 2CaCl_2 + O_2$$

(5) *By the action of concentrated sulphuric acid on manganese dioxide,* *otassium dichromate.*



$$+ 2H_2O \quad + O_2$$
$$+ 4MnSO_4 \quad + 6H_2O + 5O_2$$
$$+ 2Cr_2(SO_4)_3 \quad + 8H_2O + 3O_2$$

(6) **Laboratory Method.** Two methods commonly employed for the preparation of oxygen in the laboratory are :

(*a*) **From Potassium chlorate.** A mixture of potassium chlorate and manganese dioxide in the ratio 4 : 1 is heated in a hard glass test tube fitted with a cork and a delivery tube as shown (Fig 29·2). Oxygen evolved is collected over water. Manganese dioxide acts simply as a catalytic agent and undergoes no chemical change during the reaction (*see* Chapter 25—Catalysis).

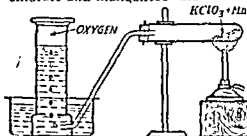
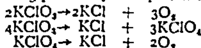


Fig. 29·2—Preparation of oxygen in the laboratory

The reactions taking place may be represented as follows :



$$2KClO_3 \rightarrow 2KCl + 3O_2$$
$$4KClO_3 \rightarrow KCl + 3KClO_4$$
$$KClO_4 \rightarrow KCl + 2O_2$$

The test tube should be kept somewhat horizontal and the manganese dioxide used should be free from carbon to avoid any explosion. *At the end of the experiment, delivery tube must be removed from under the water before heating is stopped.* This is to prevent any back suction of water into the hot tube.

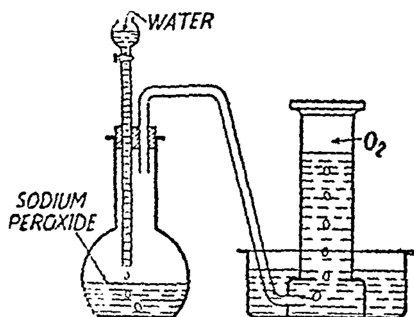
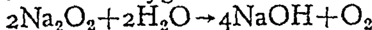


Fig. 29·3—Laboratory preparation of oxygen from oxone or oxylithe.

(*b*) **From Sodium peroxide.** Sodium peroxide used for the purpose is commercially called *Oxone* while *Oxylithe* is a 98·32% sodium peroxide mixed with iron oxide (1%) and copper sulphate (0·68%). Oxone or oxylithe is placed in a flat-bottom flask fitted with a dropping funnel and a delivery tube as shown (Fig. 29·3). Water is dropped from the dropping funnel. Oxygen evolved is collected over water.



$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

(7) **Manufacture of Oxygen.** Two main sources for the commercial preparation of oxygen are water and air. Oxygen is manufactured from these sources as given below :

(*a*) By Electrolysis of Water. *Refer to manufacture of hydrogen wherein oxygen is obtained as a by-product* (page 2·4).

(*b*) From Air. When air is liquefied and subjected to fractional evaporation, nitrogen being more volatile evaporates first leaving behind a liquid richer in oxygen. Two methods generally employed are :

(*i*) **Linde's Process.** The principle underlying Linde's process for liquefaction of gases is the **Joule-Thomson effect**—*when a gas under pressure is allowed to expand suddenly through a small orifice into a region of low pressure, it falls in temperature.* During expansion, work is done against internal attractive forces between the molecules. This results in the fall of temperature. No work is done here against external pressure. A diagrammatic sketch of the process is given in Fig. 29·4.

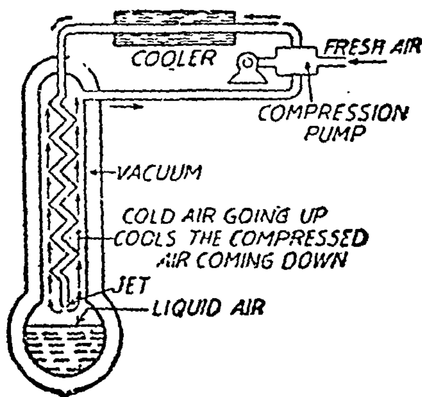


Fig. 29·4—Diagrammatic representation of Linde's process.

Process. Air free from carbon dioxide is compressed to about 200 atmospheres pressure and cooled by passing through a pipe surrounded by cold water. This cooled and compressed air passes through a spiral and escapes through a small nozzle when

it is cooled by Joule-Thomson effect. This cooled air passes up surrounding the spiral pipe and cooling the down-coming air therein. This cooled air is further cooled by expansion, and cooling is thus continued till it begins to condense. The up-going air is compressed once again and recirculated.

Oxygen is manufactured by the fractional evaporation of this liquid air by Claude's process given below :

(ii) **Claude's Process.** This is the process generally used for the manufacture of oxygen, *e.g.*, by the Indian Oxygen and Acetylene Co. Ltd. at Calcutta, Kanpur and Delhi.

Principle. When a cold compressed gas is allowed to do some external work, *e.g.*, pushing the piston of a gas engine (*adiabatic expansion*), it falls in temperature (*c.f.*, Joule-Thomson effect wherein work is done against inter-molecular forces).

Process. Air is freed from carbon dioxide, dried and then compressed. The compressed air is passed through a pipe surrounded by cold oxygen and nitrogen (Heat exchanger) where it is cooled. The cooled and compressed air is allowed to do work in an expansion engine where it is further cooled.

This cooled air now enters the plant through pipe *A* and

D, passes down through side tubes surrounded by liquid oxygen. This condenses here and collects in *C*, the condensate being 99% nitrogen + 1% oxygen.

Liquid in C is pumped through *P* to the top of the fractionating column while liquid in *B* is pumped through *P'* to a little above the middle of the fractionating column.

As the liquid falls down the fractionating column, it meets an upward stream of gases. The liquid is warmed a little as it is coming down and loses more and more of a volatile constituent, nitrogen by evaporation and gets richer and richer in oxygen. By the time it reaches the base it is 98% pure oxygen.

Similarly up-going gases lose more and more oxygen by condensation due to cooling and gets richer and richer in nitrogen. By the time the gases reach the top, it is 99% pure nitrogen which escapes through the exit provided. Liquid oxygen evaporates as it cools the air and escapes through the exit shown.

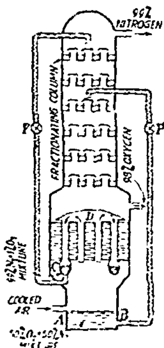


Fig. 29·5—Claude's process for the manufacture of oxygen.

The test tube should be kept somewhat horizontal and the manganese dioxide used should be free from carbon to avoid any explosion. *At the end of the experiment, delivery tube must be removed from under the water before heating is stopped.* This is to prevent any back suction of water into the hot tube.

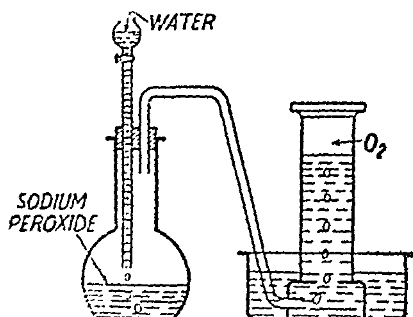
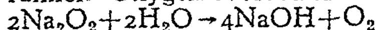


Fig. 29·3—Laboratory preparation of oxygen from oxone or oxylithe.

(*b*) From Sodium peroxide. Sodium peroxide used for the purpose is commercially called *Oxone* while *Oxylithe* is a 98·32% sodium peroxide mixed with iron oxide (1%) and copper sulphate (0·68%). Oxone or oxylithe is placed in a flat-bottom flask fitted with a dropping funnel and a delivery tube as shown (Fig. 29·3). Water is dropped from the dropping funnel. Oxygen evolved is collected over water.



$$2Na_2O_2+2H_2O \rightarrow 4NaOH+O_2$$

(7) **Manufacture of Oxygen.** Two main sources for the commercial preparation of oxygen are water and air. Oxygen is manufactured from these sources as given below :

(*a*) By Electrolysis of Water. *Refer to manufacture of hydrogen wherein oxygen is obtained as a by-product* (page 2·4).

(*b*) From Air. When air is liquefied and subjected to fractional evaporation, nitrogen being more volatile evaporates first leaving behind a liquid richer in oxygen. Two methods generally employed are :

(i) **Linde's Process.** The principle underlying Linde's process for liquefaction of gases is the **Joule-Thomson effect**—*when a gas under pressure is allowed to expand suddenly through a small orifice into a region of low pressure, it falls in temperature.* During expansion, work is done against internal attractive forces between the molecules. This results in the fall of temperature. No work is done here against external pressure. A diagrammatic sketch of the process is given in Fig. 29·4.

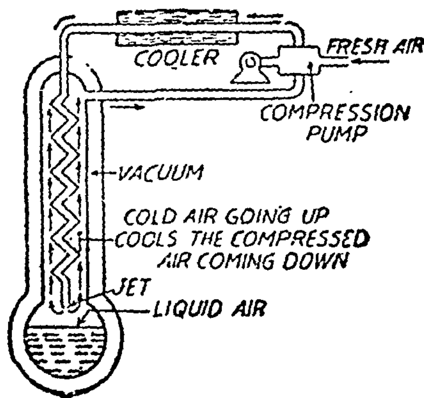


Fig. 29·4—Diagrammatic representation of Linde's process.

Process. Air free from carbon dioxide is compressed to about 200 atmospheres pressure and cooled by passing through a pipe surrounded by cold water. This cooled and compressed air passes through a spiral and escapes through a small nozzle when

it is cooled by Joule-Thomson effect. This cooled air passes up ... and cooling the down-coming air ... ther cooled by expansion, and cooling ... to condense. The up-going air is compressed once again and recirculated.

Oxygen is manufactured by the fractional evaporation of this liquid air by Claude's process given below :

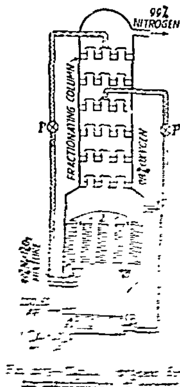
(*ii*) **Claude's Process.** This is the process generally used for the manufacture of oxygen, *e.g.*, by the Indian Oxygen and Acetylene Co. Ltd. at Calcutta, Kanpur and Delhi.

Principle. When a cold compressed gas is allowed to do some external work, *e.g.*, pushing the piston of a gas engine (*adiabatic expansion*), it falls in temperature (*c.f.*, Joule-Thomson effect wherein work is done against inter-molecular forces).

Process. Air is freed from carbon dioxide, dried and then compressed. The compressed air is passed through a pipe surrounded by cold oxygen and nitrogen (Heat exchanger) where it is cooled. The cooled and compressed air is allowed to do work in an expansion engine where it is further cooled.

This cooled air now enters the plant through pipe *A* and rises through iron tubes surrounded by liquid oxygen. A part of air gets liquefied and collects in *B* below. The condensate is 50% nitrogen+50% oxygen mixture.

The gas, which escapes condensation and collects in the space *D*, passes down through side tubes surrounded by liquid oxygen. This condenses here and collects in *C*, the condensate being 99% nitrogen+1% oxygen.



Liquid in C is pumped through *P* to the top of the fractionating column while liquid in *B* is pumped through *P'* to a little above the middle of the fractionating column.

As the liquid falls down the fractionating column, it meets an upward stream of gases. The liquid is warmed a little as it is coming down and loses more and more of a volatile constituent, nitrogen by evaporation and gets richer and richer in oxygen. By the time it reaches the base it is 98% pure oxygen.

Similarly up-going gases lose more and more oxygen by condensation due to cooling and gets richer and richer in nitrogen. By the time the gases reach the top, it is 99% pure nitrogen which escapes through the exit provided. Liquid oxygen evaporates as it cools the air and escapes through the exit ...

These gases are very cold and are used in the heat exchanger for cooling air before they are compressed into steel cylinders for sale.

4. **Physical Properties of Oxygen.**—Oxygen is a colourless, odourless and tasteless gas, slightly heavier than air and sparingly soluble in water. Solubility of oxygen in water, though small, plays an important role in the economy of nature. All aquatic animals get their oxygen needed for breathing from air that is dissolved in water in which they live.

It can be liquefied by cooling under pressure to a pale blue liquid (b.p. −183°C). On cooling the liquid in liquid hydrogen it gives a light-blue solid (m.p. −218·4°C). It cannot be solidified by rapid evaporation of the liquid as in the case of nitrogen and carbon dioxide.

5. **Chemical Properties of Oxygen.** (1) It is a divalent electronegative element, neutral towards litmus.

(2) **Oxidation reactions.** Oxygen combines with a large number of elements and compounds and the process of addition is called **oxidation.** The combination of substances with oxygen, with the evolution of heat and light, is called **combustion.** It is a particular case of oxidation. Oxygen is incombustible but a supporter of combustion.

(*a*) At Ordinary Temperature. Phosphorus is oxidised slowly in air or oxygen. Iron rusts when exposed to moist air. Breathing is only a process of oxidation of organic impurities (compounds of carbon and hydrogen) in the blood to carbon dioxide and water. Colourless nitric oxide (NO) combines with oxygen to give brown nitrogen dioxide (NO_2). Oxygen is absorbed by alkaline pyrogallol.

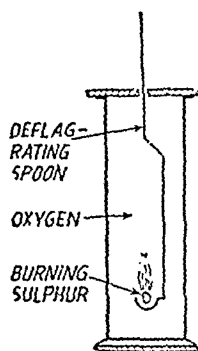


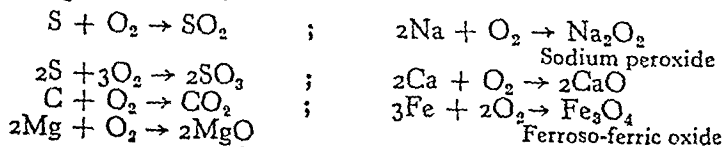
Fig. 29·6—Substances burn more brightly in oxygen.

$$P_4 + 5O_2 \xrightarrow[\text{Moisture}]{} P_4O_{10}$$

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$

$$2NO + O_2 \longrightarrow 2NO_2$$

(*b*) At Higher Temperatures. Burning phosphorus, sulphur, carbon, sodium, potassium, calcium, magnesium ribbon and iron wire burn brightly when placed in a deflagrating spoon and lowered into an oxygen cylinder. The binary compounds so obtained are **oxides.** For example, sulphur gives sulphur dioxide with traces of sulphur trioxide, carbon gives carbon dioxide, and magnesium gives magnesium oxide.



$S + O_2 \rightarrow SO_2$; $2Na + O_2 \rightarrow Na_2O_2$ (Sodium peroxide)

$2S + 3O_2 \rightarrow 2SO_3$; $2Ca + O_2 \rightarrow 2CaO$

$C + O_2 \rightarrow CO_2$; $3Fe + 2O_2 \rightarrow Fe_3O_4$ (Ferroso-ferric oxide)

$2Mg + O_2 \rightarrow 2MgO$

(*i*) Sulphur dioxide is oxidised to sulphur trioxide in the presence of vanadium pentoxide (*Contact process*).



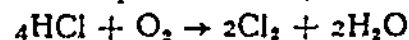
$$2SO_2 + O_2 = 2SO_3$$

(*ii*) Ammonia is oxidised to nitric oxide in the presence of platinum gauze at 800°C (*Ostwald's process*).



$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

(*iii*) Hydrochloric acid gas is oxidised to chlorine in presence of pumice stone soaked in cupric chloride (*Deacon's process*).



$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

6. **Uses of Oxygen.**—Oxygen finds use :

(*i*) *In special occupations.* Firemen, miners, deep-sea divers and aviators are equipped with self-contained oxygen apparatus to give an independent supply of pure oxygen for breathing.

(*ii*) *In hospitals.* Oxygen is given for artificial respiration to persons suffering from pneumonia or gas poisoning. Mixed with nitrous oxide or ethylene, it is used for producing anaesthesia.

(*iii*) *In welding and cutting* Oxy-hydrogen or oxy-acetylene torch is used in welding and cutting.

(*iv*) *In iron and steel industry.* Oxygen is used to increase the oxygen content of the air blast in the Bessemer and open-hearth processes.

(*v*) *In carbon dust cartridges.* Carbon dust made wet with liquid oxygen has been employed in place of dynamite in coal mining.

(*vi*) *In the laboratory and industry* oxygen is used as an oxidising agent.

7. **Tests for Oxygen.**—(*i*) A smouldering wood splinter bursts into flame in a jar of oxygen.

(*ii*) With nitric oxide it gives reddish-brown fumes of nitrogen dioxide. This is used as a distinction from nitrous oxide.

(*iii*) It is absorbed by alkaline pyrogallol.

OZONE

8. **Historical.**—Von Marum in 1785 found that a peculiar smell was felt when an electric discharge had passed in oxygen. Schonbein attributed this in 1840 to a new gas which he named ozone (Greek, *ozo*—I smell). In 1866, Soret showed that the gas was an allotrope of oxygen and assigned to it the formula O_3.

9. **Formation of Ozone.**—Ozone is formed when oxygen is exposed to ultra-violet light. This accounts for the occurrence of ozone in the upper layers of the atmosphere. It is also formed when fluorine reacts with water, when phosphorus undergoes slow oxidation in air or when water is electrolysed.

10. ***Preparation of Ozone in the Laboratory.***—*Ozone is* prepared by subjecting cold, dry oxygen to the action of silent

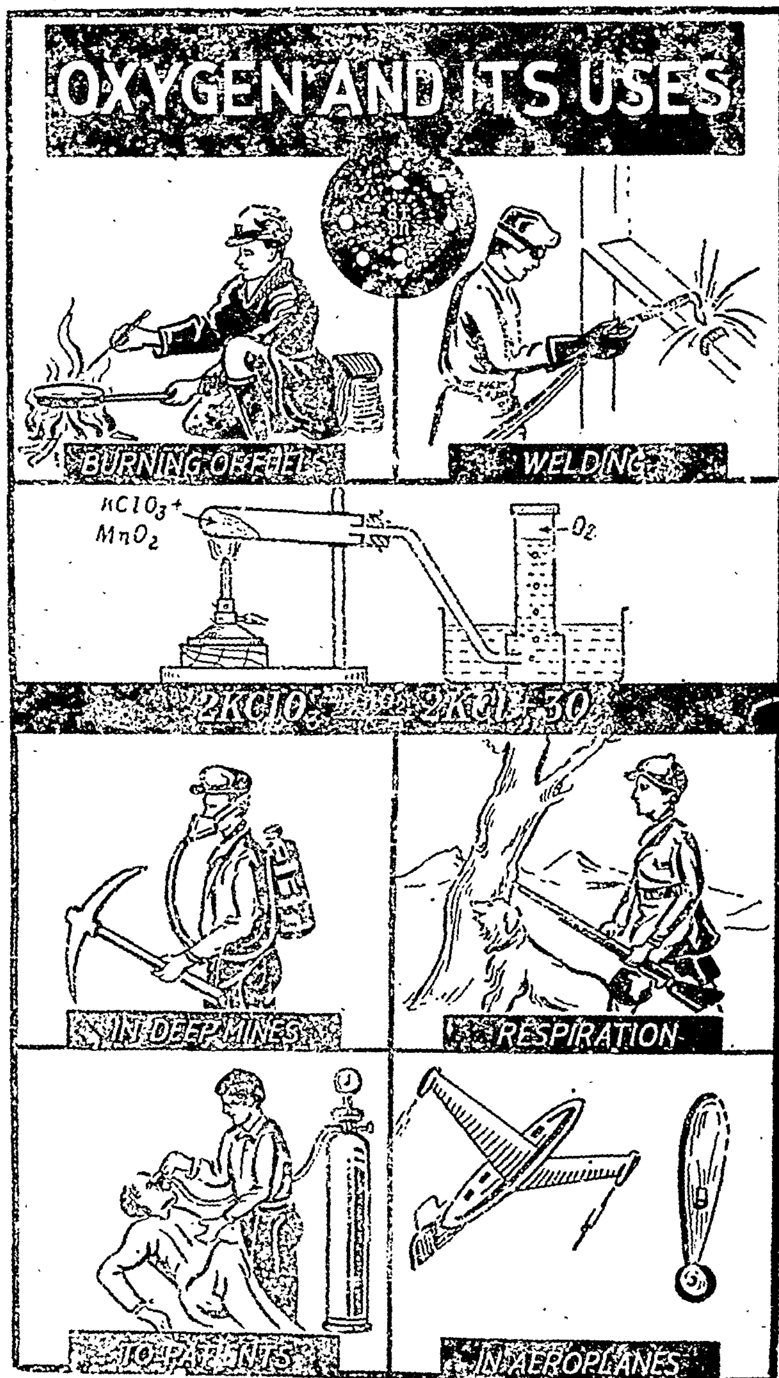

OXYGEN AND ITS USES
BURNING OF FUELS
WELDING
$KClO_3$ + MnO_2
O_2
$2KClO_3 \rightarrow 2KCl + 3O_2$
IN DEEP MINES
RESPIRATION
IN AEROPLANES

Fig. 29·7

electric discharges in an apparatus called ozoniser. Two types of ozonisers are used for its preparation in the laboratory. These are Siemen's ozoniser and Brodie's ozoniser.

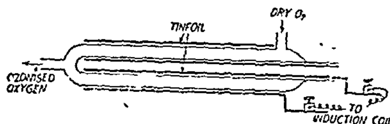


Fig. 29·8—Siemen's ozoniser.

(i) **Siemen's Ozoniser.** It consists of two co-axial glass tubes sealed at one end (Fig. 29·8). The inner surface of the inner tube and the outer surface of the outer tube are coated with tin foil. When the inner and the outer coatings are connected with the two terminals of a powerful induction coil, the gas present in the annular space is subjected to the action of silent electric discharges. Dry and cold oxygen is passed in from one end, which passes on through the annular space where it is partially converted into ozone by the action of silent electric discharges. Ozonised oxygen (10—15% ozone) comes out from the other end and is collected.

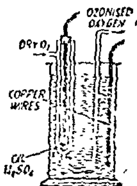


Fig. [illegible]—Brodie's ozoniser

(ii) **Brodie's Ozoniser.** *It is similar* to the Siemen's ozoniser in principle but tin foil is replaced by dilute sulphuric acid (Fig. 29·9). The copper wires dipped in sulphuric acid are connected to an induction coil. Oxygen passing through the annular space is subjected to the action of silent electric discharges and is partially converted into ozone.

11. **Manufacture of Ozone.**—For the manufacture of ozonised air, Siemens and Halske's ozoniser (Fig [illegible]) is employed. It consists of a battery of alumin[illegible] cylinders (6—8 in number) resting on an insulated glass plate and enclosed in a glass or [illegible] [illegible]. These are [illegible] [illegible] in an [illegible] [illegible] divided [illegible] [illegible] compartments. [illegible] middle [illegible] [illegible] water is [illegible] [illegible] the [illegible] The aluminium [illegible] [illegible] to a hi[illegible] [illegible]

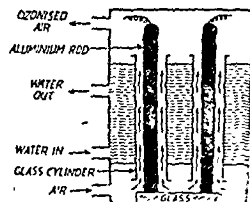


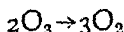
Fig. 29·10 -Siemen-Halske's ozoniser

Air is passed in the lower compartment when it is subjected to the action of silent electric discharges as it rises up through the annular spaces. Ozonised air passes out through the exit at the top and is collected.

12. **Properties of Ozone : Physical.**—It is a pale blue gas with a characteristic strong smell. When inhaled in a small amount it causes headache and nausea, in larger quantities it is poisonous. When passed through liquid oxygen, it liquefies to a deep blue liquid (b.p. −112·4°C) which can be solidified to violet black crystals (m.p. —246·7°C). It is heavier than air and is slightly soluble in water, more soluble in turpentine oil, glacial acetic acid or carbon tetrachloride.

Chemical. Chemical properties of ozone can be studied under the following heads :

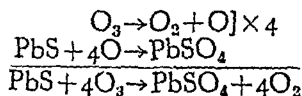
(1) **Decomposition.** Pure ozone decomposes with an explosive violence while ozonised oxygen decomposes slowly at a low temperature. It is almost instantaneous at 300°C. Presence of manganese dioxide, platinum black, copper oxide, etc., catalyses the decomposition.



$$2O_3 \rightarrow 3O_2$$

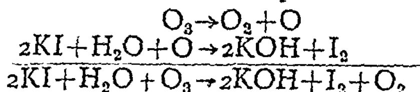
(2) **Oxidising Action.** (*a*) Due to the ease with which it can liberate an atom of nascent oxygen ($O_3 \rightarrow O_2 + O$), it acts as a powerful oxidising agent. In all these reactions corresponding to each molecule of ozone used up, a molecule of oxygen is set free. A few important examples are :

(*i*) Lead sulphide (*black*) is oxidised to lead sulphate (*white*).



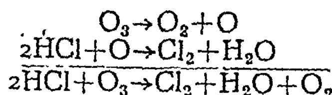
$$\begin{array}{l} O_3 \rightarrow O_2 + O] \times 4 \\ PbS + 4O \rightarrow PbSO_4 \\ \hline PbS + 4O_3 \rightarrow PbSO_4 + 4O_2 \end{array}$$

(*ii*) Iodine is liberated from potassium iodide solution.



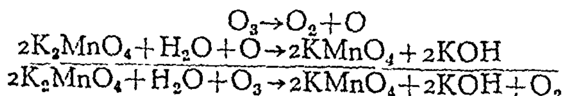
$$\begin{array}{l} O_3 \rightarrow O_2 + O \\ 2KI + H_2O + O \rightarrow 2KOH + I_2 \\ \hline 2KI + H_2O + O_3 \rightarrow 2KOH + I_2 + O_2 \end{array}$$

(*iii*) Halogen acids are oxidised to the corresponding halogens, *e.g.*, hydrochloric acid is oxidised to chlorine.



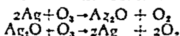
$$\begin{array}{l} O_3 \rightarrow O_2 + O \\ 2HCl + O \rightarrow Cl_2 + H_2O \\ \hline 2HCl + O_3 \rightarrow Cl_2 + H_2O + O_2 \end{array}$$

(*iv*) Potassium manganate is oxidised to potassium permanganate.



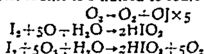
$$\begin{array}{l} O_3 \rightarrow O_2 + O \\ 2K_2MnO_4 + H_2O + O \rightarrow 2KMnO_4 + 2KOH \\ \hline 2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2 \end{array}$$

(*v*) Silver metal is blackened if warm, probably due to alternate oxidation of the metal and reduction of the oxide.



$$2Ag + O_3 \rightarrow Ag_2O + O_2$$
$$Ag_2O + O_3 \rightarrow 2Ag + 2O_2$$

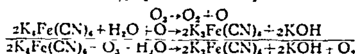
(*vi*) Moist iodine is oxidised to iodic acid (HIO_3).



$$[O_3 \rightarrow O_2 + O] \times 5$$
$$I_2 + 5O + H_2O \rightarrow 2HIO_3$$
$$I_2 + 5O_3 + H_2O \rightarrow 2HIO_3 + 5O_2$$

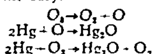
Similarly moist sulphur, phosphorus and arsenic are oxidised to their corresponding highest oxy-acids.

(*vii*) A solution of potassium ferrocyanide, $K_4Fe(CN)_6$ is oxidised to $K_3Fe(CN)_6$—potassium ferricyanide.



$$O_3 \rightarrow O_2 + O$$
$$2K_4Fe(CN)_6 + H_2O + O \rightarrow 2K_3Fe(CN)_6 + 2KOH$$
$$2K_4Fe(CN)_6 + O_3 + H_2O \rightarrow 2K_3Fe(CN)_6 + 2KOH + O_2$$

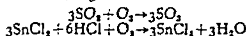
(*viii*) When passed through mercury, it loses its meniscus and sticks to glass (tailing of mercury) due to the formation of Hg_2O which dissolves in mercury.



$$O_3 \rightarrow O_2 + O$$
$$2Hg + O \rightarrow Hg_2O$$
$$2Hg + O_3 \rightarrow Hg_2O + O_2$$

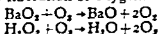
(*ix*) It is a good bleaching agent due to its oxidising action on organic matter.

(*b*) *In a few reactions*, ozone molecules as a whole is used up for oxidation, *e.g.*,



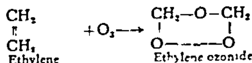
$$3SO_2 + O_3 \rightarrow 3SO_3$$
$$3SnCl_2 + 6HCl + O_3 \rightarrow 3SnCl_4 + 3H_2O$$

(3) **Reaction with Peroxides.** Reaction of ozone with barium peroxide and hydrogen peroxide results in their mutual reduction with the liberation of oxygen.



$$BaO_2 + O_3 \rightarrow BaO + 2O_2$$
$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2$$

(4) **Addition Reactions** With unsaturated organic compounds containing double bonds, it forms addition products called ozonides.



13 **Uses of Ozone.**—(*i*) As germicide and disinfectant, for sterilizing water and improving the atmosphere of crowded places—tube railways, mines and cinema halls.

(*ii*) For bleaching oils, ivory, flour, starch, etc.

(*iii*) For the manufacture of potassium permanganate by oxidation of potassium manganate.

(*iv*) In the manufacture of artificial silk and synthetic camphor.

14. **Tests of Ozone.**—Following properties of ozone are employed as tests for the gas :

(*i*) Characteristic smell.

(*ii*) It turns starch iodide paper blue.

(*iii*) *Tailing of mercury*. Mercury loses its meniscus in contact with ozone and sticks to the surface of glass.

(*iv*) A clean silver foil is blackened by ozone.

(*v*) It turns benzidine paper brown and tetramethyl base paper violet.

15. **The formula of Ozone.**—(*i*) Ozone is prepared by passing silent electric discharges through oxygen and gives oxygen on heating. This shows *it is made up of oxygen atoms and nothing else.*

(*ii*) **Soret's Experiment.** Soret enclosed over mercury equal volumes of ozonised oxygen in two flasks of equal capacity having graduated necks. In one of the flasks he introduced turpentine oil and heated the other. A decrease in volume was noticed in the first flask due to absorption of ozone. An increase in volume took place in the second flask due to the decomposition of ozone to oxygen. *The* **decrease** *in volume was found to be* **double** *the increase, e.g.*, if the increase in volume is one volume the decrease is double (=2 volumes).

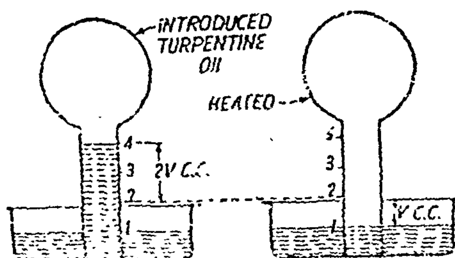
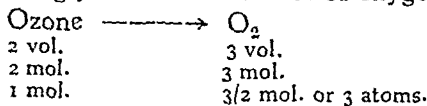


Fig. 29·11—Soret's Experiment.

Further the decrease in volume (=2 volumes) with turpentine oil is directly the volume of ozone present in the ozonised oxygen. This increases by one volume on heating when ozone (2 vol.) decomposes to give oxygen, *i.e.*, the volume of oxygen obtained= 2 vol.+1 vol.=3 vol. This shows that two volumes of ozone on decomposition by heating yield three volumes of oxygen.

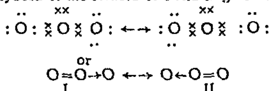


Ozone	$\longrightarrow$ O_2
2 vol.	3 vol.
2 mol.	3 mol.
1 mol.	3/2 mol. or 3 atoms.

Applying Avogadro's law, 2 mol. of ozone yield 3 mol. of oxygen or 1 mol. of ozone yields 3/2 mol. or 3 atoms of oxygen. Hence formula of ozone should be O_3.

(*iii*) Vapour density of ozone has been found to be 24 and mol. wt.=48 which corresponds to the formula O_3. *Hence O_3 is the formula of ozone.*

(iv) The ozone molecule may be represented electronically as the resonance hybrid of the structures I and II given below :



Scalar models of oxygen and ozone molecules are given in Fig. 29·12.

1Å$=10^{-8}$ cm. OXYGEN MOLECULE OZONE MOLECULE



Fig. 29·12—Scalar models of oxygen and ozone-molecules.

16. Newth's Experiment.—A more accurate determination of composition of ozone was carried out by Newth. The apparatus devised by him (Fig. 29·13) consists of two co-axial glass tubes one fitting into the other by a ground glass joint. To the outer tube is attached a manometer containing concentrated sulphuric acid coloured with indigo. A thin glass tube containing turpentine is supported, in the annular space by means of projections.

Pure oxygen is enclosed in the annular space and the inner tube is filled with dilute sulphuric acid. The apparatus is placed in an outer vessel containing ice and dilute sulphuric acid.

The oxygen is ozonised by passing silent electric discharges and contraction in volume is noted from the rise of level in the manometer. The inner tube is then twisted when the glass tube containing turpentine breaks. Ozone present is absorbed by turpentine, the contraction in volume is again read off. It will be found that first contraction in volume on ozonisation (=v c.c. say) is half the second contraction in volume on absorption (i.e., it is=$2v$ c.c.)

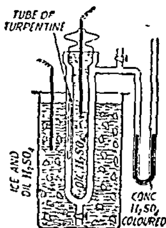


Fig 29·13—Newth's apparatus

From this $2v$ c.c. is the volume of ozone present which is absorbed by turpentine and v c.c. is the decrease in volume when oxygen gives $2v$ c.c. of ozone, i.e., $3v$ c.c. of oxygen yield $2v$ c.c. of ozone. Applying Avogadro's law to this data as in the case of Soret's experiment, we can deduce the formula of ozone.

... e atoms
... Different
... (Greek
... We shall
... phosphorus and carbon also show allotropy.

18. Position of Oxygen in the Periodic Table.—Oxygen is the first member of the Group VIA of the periodic table. Other members of the sub group being sulphur, selenium, tellurium and polonium. These are electronegative elements, each with six valency electrons as given in the table below :

Element	*Atomic Number*	*Electronic Configuration*
Oxygen	8	2, 6
Sulphur	16	2, 8, 6
Selenium	34	2, 8, 18, 6
Tellurium	52	2, 8, 18, 18, 6

They tend to gain two electrons to form the negative ions : O^{2-} (oxide) S^{2-} (sulphide) and Se^{2-} (selenide) etc. They are typical non-metals and exist in different allotropic forms. All of them form binary compounds with hydrogen.

TEST YOURSELF ON THESE REACTIONS

Write equations of the reactions, if any, between :

1. Action of heat on (i) Potassium chlorate, (ii) Potassium nitrate, (iii) Potassium permanganate, (*iv*) Mercuric oxide, (*v*) Red lead, (*vi*) Silver oxide (*vii*) Manganese dioxide, (*viii*) Barium peroxide, (*ix*) Ozone.

2. Sodium peroxide+water.

3. Conc. sulphuric acid+(i) Manganese dioxide, (ii) Potassium permanganate, (iii) Potassium dichromate.

4. Catalytic oxidation of (i) Sulphuric dioxide, (ii) Ammonia, (iii) Hydrogen chloride.

5. Ozone+(i) Lead sulphide, (ii) Potassium iodide, (iii) Hydrochloric acid, (*iv*) Potassium manganate, (*v*) Silver, (*vi*) Moist iodine, (*vii*) Potassium ferrocyanide, (*viii*) Mercury, (*ix*) Sulphur dioxide, (*x*) Stannous chloride (acidified), (*xi*) Barium peroxide, (*xii*) Hydrogen peroxide, (*xiii*) Ethylene.

QUESTIONS

Essay-type Questions

1. Give a brief description of the methods used in the manufacture of oxygen from (*a*) water, (*b*) air. What are its uses ?

How would you distinguish between oxygen and nitrous oxide ?

Oxygen helps fire burn. Water contains 89% oxygen. In view of these two facts account for the seemingly contradictory use of water as a fire extinguisher.

2. How would you prepare ozone in the laboratory ? What is its action on (i) lead sulphide, (ii) hydrogen peroxide, (iii) potassium iodide solution, (*iv*) sulphur dioxide, and (*v*) hydrobromic acid.
(*Punjab Pre-Univ. 1971 ; Delhi H.S. 1971, 68*)

3. Describe the manufacture of ozone. Discuss its important uses. What is the action of ozone on (i) mercury, (ii) potassium iodide, (iii) ethylene?
(*Kashmir Inter. 1961*)

4. Compare the properties of ozone with those of (i) Oxygen, and (ii) Hydrogen peroxide. (*Delhi H.S. 1962 ; Punjab Inter. 1961*)

5. Describe a method for the preparation of ozone in which it differs from oxygen. Describe an experiment to prove that the molecular formula of ozone is O_3.
(*Delhi H.S. 1972*)

6. Explain the term allotropy. On what grounds has it been concluded that ozone is an allotropic form of oxygen ? (*Delhi H.S. 1967*)

7. Describe the preparation and properties of ozone. How has the formula of ozone been determined ? (*Delhi H.S. 1964 ; M.P. Inter. 1964*)

8. The weight of one litre (at N.T.P.) of a mixture of oxygen and ozone was 1·500 gm. On shaking 100 c.c. (at N.T.P.) of this mixture with turpentine the volume became 90 c.c. (at N.T.P.) Deduce the molecular weight of ozone from the above data.

9. What are the principles on which the modern process for the Liquefaction of permanent gases is based? (*Delhi Pre-Medical 1961*)

[Hint. Discuss Joule-Thomson effect and Adiabatic expansion as given on page 216.]

10. Describe briefly a purely physical process by which oxygen can be prepared on a large scale.

When oxygen is produced by heating a mixture of potassium chlorate and manganese dioxide, how would you show that oxygen comes from potassium chlorate and not from manganese dioxide?

What is the difference between oxygen and ozone? (*Delhi H.S. 1964*)

Test Your Understanding

11. Fill in the blanks in the following:

(i) During fractional evaporation of liquid air, ...being .....evaporates first.

(ii) Oxygen is absorbed by an alkaline solution of......

(iii) Ozone is soluble in .....

(iv) Oxygen partially changes into ozone when subjected to the action of......

(v) Ozone forms an......called .....with ethylene.

KEY

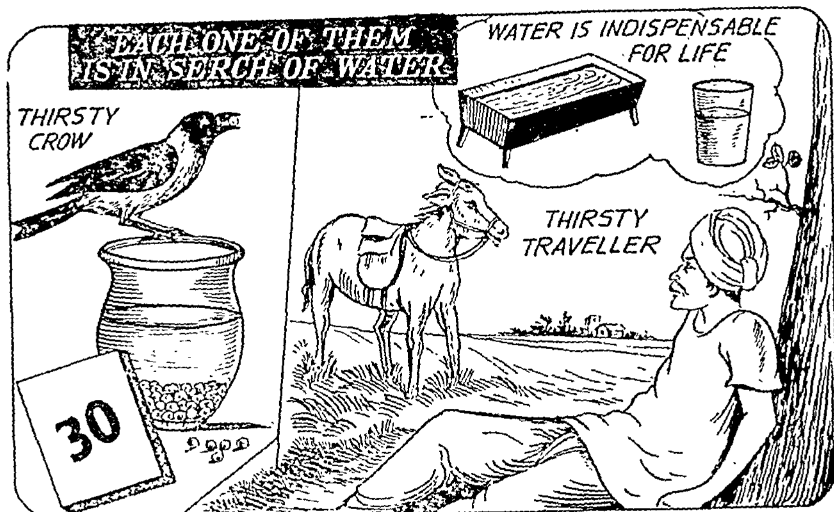
(i) nitrogen, more volatile;

(ii) pyrogallol;

(iii) turpentine;

(iv) silent electric discharges;

(v) addition product, ethylene ozonide.



Water and Hydrogen Peroxide

WATER

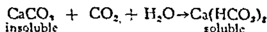
1. **Historical.**—Water is one of the most abundant and important substances known to man. It was considered to be an element for a long time till Cavendish, an English physicist, prepared water in 1781 by combining hydrogen and oxygen. Later on Lavoisier decomposed water by passing steam over red hot iron. He thus proved that water was not an element but a compound of hydrogen and oxygen.

2. **Occurrence.**—Water is everywhere. It is present in the air as water vapour and it is in the ground in the form of underground streams. Surface water in the form of oceans, rivers and lakes covers about three-quarters of the earth's crust. It is an essential constituent of all animal and vegetable matter, *e.g.*, all foods contain as much as 60 to 70 per cent water while human body contains 70 per cent of it. In the combined state it is present in many salts as water of crystallization.

3. **Natural Waters.**—Water has a great solvent action. It dissolves solids, liquids and gases. Pure water is therefore, never found in nature. It is found in the following forms :

(1) **Rain water.** Water is constantly vaporising from the sea. Water vapours rise up to higher altitudes where they condense and fall down as rain. Rain water thus being a sort of distilled water is the purest form of the natural waters. During its fall; it dissolves gases like carbon dioxide, sulphur dioxide, ammonia, and dust particles from the atmosphere. First showers are fairly impure but the subsequent showers are found to be very pure and used in place of distilled water sometimes.

(2) **Surface Water.** Rain water runs off the ground as surface water. It flows in streams or rivers to the sea. It contains dissolved salts, organic matter and suspended impurities, *e.g.*, clay. Carbon dioxide present enables it to dissolve carbonates in the soil.



$$\underset{\text{insoluble}}{CaCO_3} + CO_2 + H_2O \rightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$$

Such waters containing dissolved calcium bicarbonates sometimes trickle from the roof of caves. The falling drops lose carbon dioxide and deposit calcium carbonate.



$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

With the lapse of time beautiful pillars are found to have been formed. Those hanging from the roof are called Stalactites while others that have arisen from the floor are known as Stalagmites.



Fig. 30·1—Stalactites and Stalagmites.

(3) **Spring or Deep well water.** Rain water which percolates through the soil till it reaches an impervious rock, constitutes an underground stream of water. At places it reaches the surface again and issues out as *spring water*. At other places wells are sunk in the earth to get water. The suspended matter is largely removed and the water is clear as it has filtered through the porous soil. Organic matter and nitrogen compounds are usually absent as they are oxidised by soil bacteria. Spring or well water is suitable for drinking purposes except in certain cases where large amounts of dissolved impurities are present.

(4) **Mineral waters.** Certain springs contain special constituents not present in ordinary water. These are called mineral springs and their waters are known as mineral waters. Many of them are of medicinal value. For example,

(*a*) *Chalybeate waters* contain iron as ferrous bicarbonate and are good tonics.

(*b*) *Heptic waters* contain hydrogen sulphide and alkali sulphides and cure skin diseases. Important sulphur springs in Northen India are at Jawalamukhi (Kangra), Tatta Pani (Simla), Sohna (Gurgaon).

(*c*) *Bitter waters* contain various salts, *e g.*, sodium sulphate, magnesium sulphate and are good laxatives.

(*d*) *Alkaline waters* contain sodium, bicarbonate and sometimes lithium bicarbonate which is beneficial for gout.

(5) Sea water. Biggest source of natural water is the sea. It [illegible] of dissolved solids with [illegible]. Other salts present are [illegible] carbonates of magnesium calcium and potassium. Traces of iodides present are absorbed by certain sea-seeds. Percentage of the dissolved salts is much higher in land-locked seas, *e.g.*, 23% in the Dead Sea. With this high content of dissolved salts all animals die in it and hence the name.

4. **Physical Properties of Water.**—It is a colourless, odourless and tasteless liquid (m.p. 0°C; b.p. 100°C). Its maximum density is 1 at 4°C. Melting and boiling points of water are abnormally high as compared with hydrogen compounds of other elements of oxygen family. It is our most important solvent. Pure water is a bad conductor of electricity.

Anomalous Behaviour of water. In ice, the water molecules are united through hydrogen bonds to give giant molecules of the composition $(H_2O)_x$ where x is a very large number. Water molecules in ice are packed closely together but are held in a relatively open crystal structure by hydrogen bonds. This is responsible for the low density of ice. On melting the ice structure collapses and molecules become closely packed causing increase of density. On heating there is further breaking up of the associated water molecules resulting in a closer packing of molecules and further diminishing of volume and increase in density. Above 4°C the expansion due to increased motion of the molecules becomes greater than the contraction due to breaking up of the hydrogen bonds and the liquid expands. In the vapour form the kinetic energy of the molecules is too much for effective bonding to occur and molecules conform to the simple formula, H_2O.

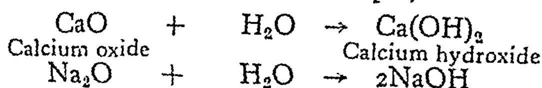
The existence of hydrogen bonds between water molecules is also responsible for its abnormally large specific heat and the latent heats of fusion and vaporization. When ice is melted, water is heated or vaporized, heat is required for overcoming the weak attraction between the molecules (van der Waals forces) as well as for breaking the hydrogen bonds. Hence more energy is needed for these operations in water than in any other analogous substance wherein there is no hydrogen bonding.

5. **Chemical Properties.**—The chemical properties of water can be discussed from nine points of view as given below :

(*i*) **Stability.** It is very stable and does not decompose easily. Decomposition of water is not more than 2% even when heated to as high a temperature as 2000°C.

(*ii*) **Behaviour with Metals.** (*See* page 2·2).

(*iii*) **Reactions with Metallic Oxides.** Water combines with metallic oxides to form bases. For example,

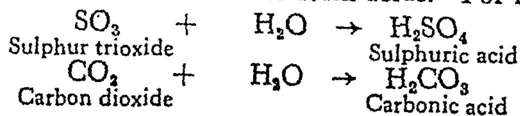


$$\underset{\text{Calcium oxide}}{CaO} + H_2O \rightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2}$$

$$Na_2O + H_2O \rightarrow 2NaOH$$

The oxides of metals which react with water to form bases are called **basic anhydrides** (*bases without water*).

(*iv*) **Reactions with oxides of Non-metals.** With non-metallic oxides water combines to form acids. For instance,

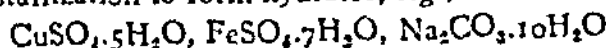


$$\underset{\text{Sulphur trioxide}}{SO_3} + H_2O \rightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$\underset{\text{Carbon dioxide}}{CO_2} + H_2O \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

The oxides of non-metals which unite with water to form acids are called acid anhydrides.

(*v*) **Water of hydration.** It combines with many salts during crystallization to form hydrates, *e.g.*,

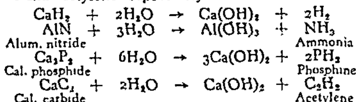


$$CuSO_4.5H_2O,\ FeSO_4.7H_2O,\ Na_2CO_3.10H_2O$$

The water present in the hydrates is called water of hydration or water of crystallization. The crystalline shape of the crystals and sometimes their colour also is due to this water of crystallization. On heating, the water of crystallization is driven off and *anhydrous salts* are left behind.

(*vi*) **Water as a Catalyst.** Water acts as an effective catalyst in many reactions. Perfectly dry gases invariably fail to react and a trace of moisture is enough to promote chemical changes.

(*vii*) **With hydrides, nitrides, phosphides and carbides.** Water reacts with these compounds to liberate hydrogen, ammonia, phosphine and acetylene respectively.



$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

$$\underset{\text{Alum. nitride}}{AlN} + 3H_2O \rightarrow Al(OH)_3 + \underset{\text{Ammonia}}{NH_3}$$

$$\underset{\text{Cal. phosphide}}{Ca_3P_2} + 6H_2O \rightarrow 3Ca(OH)_2 + \underset{\text{Phosphine}}{2PH_3}$$

$$\underset{\text{Cal. carbide}}{CaC_2} + 2H_2O \rightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

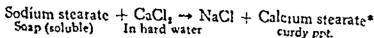
(*viii*) **Causes Ionization.** Water causes acids, bases and salts to dissociate and give ions (See Chapter 22).

(*ix*) **Causes Hydrolysis.** Water brings about hydrolysis of salts, weak acids or weak bases (*See* page 1·218).

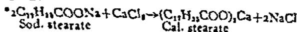
6. **Test for Water.**—Anhydrous copper sulphate (*white*) turns blue in contact with water. The fact is used as a test for water.

7. **Hard and Soft Water.**—A sample of water containing soluble salts of calcium, magnesium or iron is called "*hard water*" as it is "hard" to get lather when soap is added to such a sample of water. On the other hand, the sample of water is termed "*soft water*" when it lathers readily with soap.

Soap is the sodium salt of a higher fatty acid, *e.g., sodium* stearate. The sodium salt is soluble in water but the corresponding calcium, magnesium or iron salts are insoluble in water. When soap is added to soft water, it dissolves and lathers readily. On adding soap solution to a sample of hard water which contains calcium or magnesium ions, soap is precipitated as insoluble salts of these metals. No lather is obtained until all these ions are removed.



$$\underset{\text{Soap (soluble)}}{\text{Sodium stearate}} + \underset{\text{In hard water}}{CaCl_2} \rightarrow NaCl + \underset{\text{curdy ppt.}}{\text{Calcium stearate*}}$$



*$$\underset{\text{Sod. stearate}}{2C_{17}H_{35}COONa} + CaCl_2 \rightarrow \underset{\text{Cal. stearate}}{(C_{17}H_{35}COO)_2Ca} + 2NaCl$$

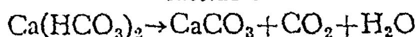
Hardness of water due to the presence of bicarbonates of calcium or magnesium is called temporary hardness, while presence of sulphates and chlorides of calcium and magnesium cause permanent hardness.

8. **Water Softening.**—Methods employed for softening water are different depending upon the fact whether the hardness is temporary or permanent. The temporary hardness can be removed in any of the following ways :

(*i*) **Boiling.** The soluble bicarbonates decompose on boiling and are precipitated as carbonates which are allowed to settle and are filtered off.

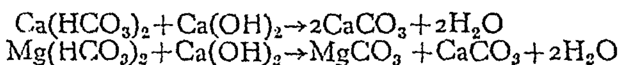


$$Mg(HCO_3)_2 \rightarrow \underset{\text{insoluble}}{MgCO_3} + CO_2 + H_2O$$



$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

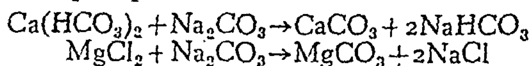
(*ii*) **Clark's Method.** By the addition of a calculated quantity of milk of lime, the soluble bicarbonates are converted into insoluble carbonates which settle to the bottom and are removed.



$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O$$

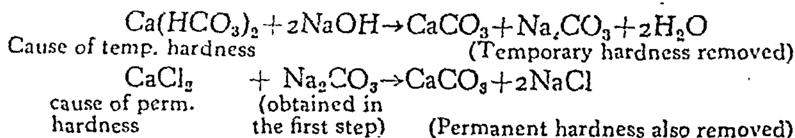
The following methods used for removing temporary hardness can also be employed for **removing permanent hardness** :

(*iii*) *By adding washing soda* when the calcium or magnesium salts present are precipitated as carbonates.



$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaHCO_3$$
$$MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 + 2NaCl$$

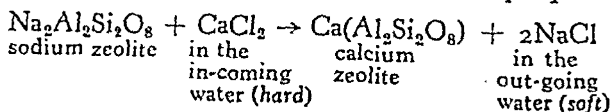
In case temporary hardness and permanent hardness are present together, water is softened by addition of caustic soda.



$$\underset{\text{Cause of temp. hardness}}{Ca(HCO_3)_2} + 2NaOH \rightarrow CaCO_3 + Na_2CO_3 + 2H_2O \quad \text{(Temporary hardness removed)}$$

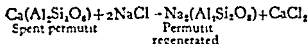
$$\underset{\text{cause of perm. hardness}}{CaCl_2} + \underset{\text{(obtained in the first step)}}{Na_2CO_3} \rightarrow CaCO_3 + 2NaCl \quad \text{(Permanent hardness also removed)}$$

(*iv*) **Permutit process.** Permutit is an artificial zeolite. Chemically it is a sodium aluminium orthosilicate ($Na_2Al_2Si_2O_8.xH_2O$) obtained in the form of a coarse sand by fusing together sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2). Permutit is packed in a suitable container (Fig. 30·2) and hard water is allowed to percolate through it when *calcium and magnesium salts present in hard water are replaced by sodium salts which are harmless.* Thus the water is softened and taken out from the tap T_1.



$$\underset{\text{sodium zeolite}}{Na_2Al_2Si_2O_8} + \underset{\text{in the in-coming water (hard)}}{CaCl_2} \rightarrow \underset{\text{calcium zeolite}}{Ca(Al_2Si_2O_8)} + \underset{\text{in the out-going water (soft)}}{2NaCl}$$

When the apparatus has been in use for about 12 hours, nearly whole of permutit gets exhausted. It is regenerated for subsequent use by soaking it with 10% brine (NaCl) and then washing away the chlorides. The washings are removed through the tap T_2 near the base.



$$Ca(Al_2Si_2O_8)+2NaCl \rightarrow Na_2(Al_2Si_2O_8)+CaCl_2$$

Spent permutit — Permutit regenerated

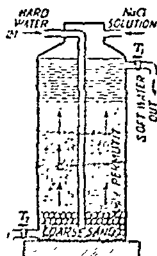
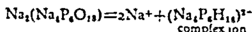


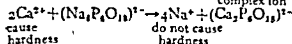
Fig. 30·2—Permutit Process for water softening.

(v) Calgon process. Calgon is the trade name given to a complex salt, sodium hexametaphosphate $(NaPO_3)_6$ or $Na_2(Na_4P_6O_{18})$. It has recently been used in softening water for boiler use. Calcium or magnesium salts present in hard water react with calgon to give complex negative ions $(Ca_2P_6O_{18})^{2-}$ or $(Mg_2P_6O_{18})^{2-}$.



$$Na_2(Na_4P_6O_{18})=2Na^{+}+(Na_4P_6H_{18})^{2-}$$

complex ion



$$2Ca^{2+}+(Na_4P_6O_{18})^{2-}\rightarrow 4Na^{+}+(Ca_2P_6O_{18})^{2-}$$

cause hardness — do not cause hardness

The formation of complex negative ions decreases the concentration of the calcium ions, thus reducing the hardness of water. Calgon not only prevents the precipitation of soap as calcium salt of higher fatty acids (calcium soaps) but actually dissolves such soaps. It has, therefore, found wide use in laundry for removing calcium soap which would otherwise encrust the washed textiles.

Soft water free from Ca^{2+} and Mg^{2+} →

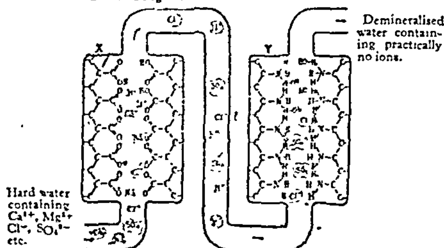
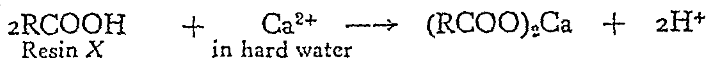


Fig. 30·3—Softening of water by Ion-exchange Resins.

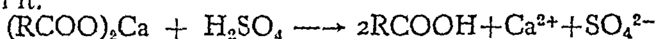
(*vi*) **With Ion-exchange Resins.** Recently ion-exchange resins have been employed to remove all minerals from water. Water is allowed to flow through a tank partly filled with the granules of a resin *X* which absorbs positive ions. Water flowing out of this tank does not contain any ions like calcium, magnesium, *i.e.*, it is soft water.

Resin *X* consists of giant organic molecules arranged in the form of porous framework having acidic groups (carboxyl groups, COOH) attached to it. Ca^{2+} and Mg^{2+} ions present in hard water are removed by the acidic framework and H^+ ions are added to water.



$$\underset{\text{Resin } X}{2RCOOH} + \underset{\text{in hard water}}{Ca^{2+}} \longrightarrow (RCOO)_2Ca + 2H^+$$

After use the giant molecules of resin *X* can be regenerated by passing a moderately concentrated solution of sulphuric acid through it.

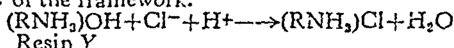


$$(RCOO)_2Ca + H_2SO_4 \longrightarrow 2RCOOH + Ca^{2+} + SO_4^{2-}$$

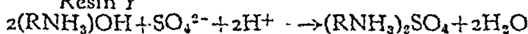
If it is further passed through another resin *Y* which absorbs negative ions, it gets completely demineralized and is as good as distilled water.

Resin *Y* contains grains of giant organic molecules (substituted ammonium hydroxide) with basic groups (OH) attached to it.

The electronegative ions present in the in-coming water are held by the ammonium ions of the framework.



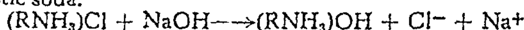
$$\underset{\text{Resin } Y}{(RNH_3)OH} + Cl^- + H^+ \longrightarrow (RNH_3)Cl + H_2O$$



$$2(RNH_3)OH + SO_4^{2-} + 2H^+ \longrightarrow (RNH_3)_2SO_4 + 2H_2O$$

Thus the out-going water contains practically no ions and can be used in place of distilled water.

Resin *Y* can be regenerated by treating with moderately concentrated solution of caustic soda.



$$(RNH_3)Cl + NaOH \longrightarrow (RNH_3)OH + Cl^- + Na^+$$

(*vii*) Softening can also be effected by distillation which removes all soluble salts present.

9. **Purification of water for Laboratory use.**—Water needed in the laboratory for analytical purposes should be free from suspended and dissolved impurities. These are removed by a process of distillation, a process consisting of evaporation followed by condensation of vapours in a separate vessel.

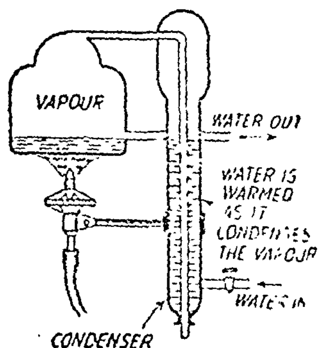


Fig. 30·4—A continuous action distillation still.

This type of apparatus used for distillation in the laboratory is shown in Fig. 30·4. Water is heated in a copper still and the vapours passed through a tube surrounded by in-coming water which is warmed before it enters the still thus economising fuel.

Recently ion exchange process has been introduced. This gives water of equivalent purity.

10. Potable Water.—For drinking purposes we do not need water of such high purity as for laboratory use. This would not only be expensive but would actually be less pleasant in taste. Potable water should be—

(i) colourless and odourless ;

(ii) clear, *i.e.*, free from suspended matter ;

(iii) free from harmful bacteria ;

(iv) free from impurities of an injurious nature, *e.g.*, nitrites, nitrates and ammonia.

It should not contain excessive amounts of undesirable dissolved solids. Small quantities of salts and air dissolved in water, however, give it the usual pleasant taste and supply a portion of the mineral constituents necessary for the body growth.

[illegible] *always unfit for* [illegible] might contain [illegible] mpounds, which [illegible] *er is not always* [illegible]

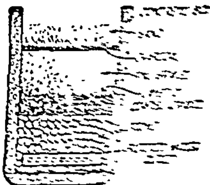
11. Purification of water for drinking purposes.—The purification of water needed for drinking purposes in towns and cities is an important practical problem for the chemist. The actual methods employed vary with the local conditions but all aim at (i) *removing the suspended impurities; and* (ii) *destroying the bacteria.*

Different methods employed to remove suspended matter are :

(1) Sedimentation or Settling. Water is allowed to stand in big tanks or reservoirs when most of the suspended matter settles to the bottom. Decanted water is taken from outlets located at convenient points. This may be further purified if necessary

(2) Addition of Chemicals followed by Settling [illegible] suspended impurities are colloidal in nature. These are [illegible] agulated by addition of chemicals like alum. The prec[illegible] to the bottom dragging bacteria and other tiny particles [illegible]

(3) Filtration. Water is filtered through layers [illegible] gravel and charcoal several feet thick. Charcoal serves [illegible] the colouring matter while sand and gravel remove the suspended matter. A common sand filter is shown in Fig. 30·5. A thin layer, deposited at the top of sand as a result of sedimentation, increases the efficiency of the filter and strains out bacteria. Thick layers, however, retard filtration and have to be removed.



In some household filters (Fig. 30·6) water is

filtered through porous tubes made of unglazed procelain. The filter is cleaned daily to remove the deposit, otherwise the bacteria multiply in it and the water passing through is rather polluted than purified.

Fig. 30·6 – Porcelain filter for household.

Various methods adopted for destroying bacteria are :

(1) **Aeration.** On simple exposure or when sprayed in air, water absorbs oxygen which oxidises the organic matter. This is the natural process by which a contaminated stream purifies itself after flowing a sufficient distance.

(2) **Exposure to Sunlight or Ultra-violet light.** Sunlight also is helpful in destroying bacteria but it cannot penetrate large depths of water. It is, therefore, not an efficient method for purification of water. Ultra-violet light from a mercury vapour lamp destroys bacteria quite effectively. Water in swimming pools is kept clean by installing some mercury vapour lamps under water.

(3) **Boiling.** Boiling of water for 15—20 minutes destroys all disease-producing bacteria but it is not possible to purify large volumes of water by boiling. In the household, contaminated water may be rendered perfectly safe by boiling.

(4) **Chlorination.** Addition of liquid chlorine or bleaching powder in small quantities is a very effective method of sterilizing water.

(5) **Ozonization.** Ozone is bubbled through water or a current of ozone is passed up a tower through which water is percolating. It destroys bacteria and leaves no harful products behind.

(6) **Addition of Copper sulphate.** Small quantities of copper sulphate destroy the microscopic plants known as algae. These are frequently present in water and impart an odour and colour to it.

12. **Water for Washing purposes.**—Hard water cannot be used for washing purposes. It is a nuisance for laundry work as large quantities of soap are wasted in giving sticky precipitates with the calcium and magnesium ions present in hard water (*see* page 2·32). Moreover, the precipitates stick to the fibres of the garments being laundered. For bathing also we need soft water which lathers freely with soap.

13. **Water for Boiler use.**—Hard water cannot be used for generating steam in boilers on account of the following reasons :

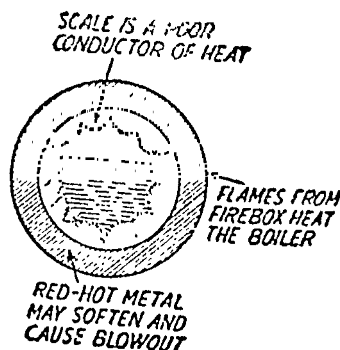
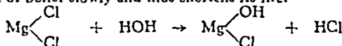


Fig. 30·7—Formation of scale inside the boiler with hard water.

(i) **Loss of Heat.** Hard water on boiling precipitates calcium carbonate which collects as a hard scale on the inside of the boiler and the steam pipes (*see* Fig. 30·7). A thick crust of the scale thus deposited acts as heat insulator and causes loss of heat.

(ii) **Danger of explosion.** The metal of the boiler in contact with fire becomes red hot and expands away from the scale due to overheating when sufficient water is not there in it. The hot scale cracks in contact with cold water which percolates through the cracks and is suddenly converted into steam as it falls on the red hot surface. The huge pressure thus produced may cause the boiler to burst.

(iii) **Corrosion.** The chlorides of calcium or magnesium are hydrolysed to produce hydrochloric acid which corrodes the surface of boiler slowly and thus shortens its life.



$$Mg\langle^{Cl}_{Cl} + HOH \rightarrow Mg\langle^{OH}_{Cl} + HCl$$

Sea-water cannot be used for boiler use because it contains magnesium chloride which decomposes to give free hydrochloric acid as given above resulting in shortening of the boiler's life due to corrosion.

14. **Water for Irrigation purposes.**—Water is essential for plant growth. Plants get this water from the soil. During rains this water is stored in the soil. When the rains fail, water is given to the soil by artificial means—from wells and canals. Water used for irrigation must be neutral and should not contain more than 0·1% of dissolved salts.

If the water used for irrigation is not neutral and contains more than 0·1% salts, the fertility of the soil decreases. Slowly the soil becomes saline and unsuitable for most of the crops.

Some crops, however, grow well in saline soils, *e.g.*, tobacco. These crops should be grown when the soil becomes saline.

15. **Composition of Water by Weight.** Two methods used for finding the composition of water by weight are :

(i) **By Indirect Weighings.** The method was originally devised by Jeans Dumas (1800-84), a French chemist. Hydrogen is dried by passing through a calcium chloride tube and passed over a weighed quantity of copper oxide heated in a hard glass tube (Fig. 30·8). The oxide is reduced to metallic copper while hydrogen is oxidised to water. The water vapour is absorbed in a weighed calcium chloride tube.

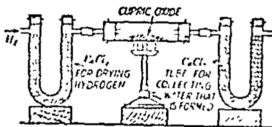


Fig. 30·8—Dumas' method for finding the composition of water by weight

Increase in weight of calcium chloride tube (=x, say) gives the weight of water formed, while decrease in weight of copper oxide

(=y, say) gives the weight of oxygen combined with hydrogen to give water. Difference between these two weights (=$x-y$) gives the weight of hydrogen which combines with y parts by weight of oxygen. From this data we can see that one gram of hydrogen combines with 7·94 grams of oxygen to give 8·94 grams of water.

(*ii*) **By Direct Weighings.** This is more accurate method devised by Morley in 1895. Oxygen gas was purified, collected in an evacuated globe and weighed. Similarly hydrogen was purified,



Edward William Morley
(1838 – 1923)
American chemist and physicist; best known for his work on determining the composition of water by weight.

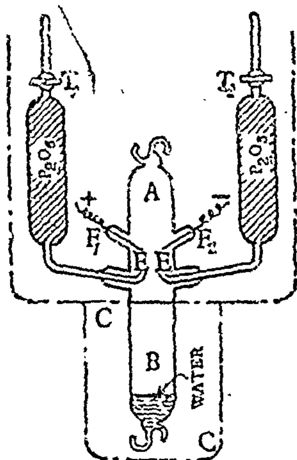


Fig. 30·9—Morley's method f finding composition of water l weight.

absorbed in palladium contained in a globe and weighed. The tw gases were led into a combustion chamber A through the jets E (Fig. 30·9). Their flow was carefully regulated by taps T_1 and T The gases combined to give water when electric sparks wei passed through the terminals F_1 F_2. When sufficient water wa obtained, it was weighed. Weights of hydrogen and oxyge combined were ascertained from the loss in weight of the glob containing them. From this the composition of water was ca culated.

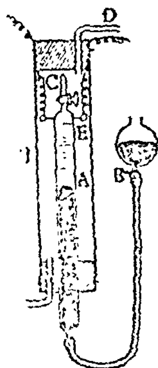
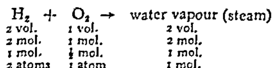


Fig. 30·10.

16. Composition of Water by Volume.

(*i*) *Synthetic Method.* *Mixture of one volum of oxygen with six volumes of hydrogen is taken i* a eudiometer tube A surrounded by a jacket J i which vapours of amyl alcohol (b.p. 130°C) a passed from above. Electric sparks are passe through the mixture when hydrogen and oxyge combine to give water vapour. The volume of tl residual gases is found to be six volumes which further reduced to four volumes (found to be hy drogen) on cooling. From this we find that tw volumes of hydrogen combine with one volume oxygen to give two volumes of steam.



H_2	+	O_2	→	water vapour (steam)
2 vol.		1 vol.		2 vol.
2 mol.		1 mol.		2 mol.
1 mol.		½ mol.		1 mol.
2 atoms		1 atom		1 mol.

Applying Avogadro's law we find that 2 mol. of hydrogen combine with 1 mol. of oxygen to give 2 mol. of water.

Or the molecule of water is made up of 1 mol. (=2 atoms) of hydrogen and ½ mol. (=1 atom) of oxygen, *i.e.*, its formula is H_2O.

Its vapour density has been found to be 9 which gives molecular weight of water as 18. This agrees with the formula of water as H_2O.

(ii) *Analytical Method.* Water is acidulated and decomposed by the use of an electric current in a voltameter (Fig. 30·11). It is found that the two gases, hydrogen and oxygen, are collected in the volume ratio 2 : 1. Applying Avogadro's law we conclude that 2 mol. of hydrogen combine with 1 molecule of oxygen. Or 1 mol. (=2 atoms) of hydrogen combines with ½ mol. (=1 atom) of oxygen.

Empirical formula of water is, therefore, H_2O. Its molecular formula may be written as $(H_2O)_x$ with mol. wt.$=18x$. Mol. wt. as determined from its V. D. data is 18. Equating the two molecular weights, we have

$$18x=18 \quad \text{whence} \quad x=1.$$

∴ Molecular formula of water is H_2O.

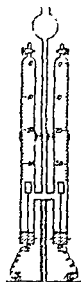


Fig 30·11.

17. **Structure of Water Molecule** —The bonds between oxygen and hydrogen atoms in water are covalent bonds. Furthermore the water molecule

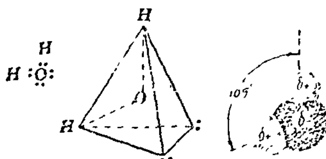


Fig 30·12.

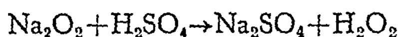
18. **Heavy Water.** – Deuterium oxide is called heavy water and written as D_2O or ^2H_2O. It has a freezing point of 3·8°C and a b.p. of 101·42°C with a maximum density of 1·1073 at 4°C. Latent heat of vaporization of heavy water is 53·3 calories per gram. On electrolysis of water, small residue left is mainly heavy water.

HYDROGEN PEROXIDE

19. **Historical and Occurrence.**—Hydrogen peroxide was obtained by L.J. Thenard, a French chemist, in 1818, by the action of dilute acids on barium peroxide. He named it *oxygenated water*. Traces of hydrogen peroxide are present in the atmosphere and traces of it are reported to be present in plants.

20. **Preparation.**—Hydrogen peroxide is prepared by the action of acid on a suitable metallic peroxide. Different methods commonly employed for the purpose are :

(1) **By the action of dilute sulphuric acid on sodium peroxide.** Calculated quantity of sodium peroxide is added in small proportions to a 20% ice-cold solution of sulphuric acid, with which it reacts as follows :



$$Na_2O_2+H_2SO_4 \rightarrow Na_2SO_4+H_2O_2$$

Crystals of $Na_2SO_4.10H_2O$ separate out on cooling and a 30% solution of hydrogen peroxide is obtained. The solution still contains some sodium sulphate but it does not interfere with some of the common uses of hydrogen peroxide. A pure sample of hydrogen peroxide free from sodium sulphate may, however, be obtained by vacuum distillation (*see under Concentration*).

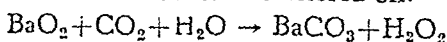
(2) **From Barium Peroxide.** To prepare a pure sample of hydrogen peroxide free from metallic salts, barium peroxide is reacted with an acid which forms an insoluble barium salt such as sulphuric acid or carbonic acid, as given below :

(*i*) *By the action of dilute sulphuric acid on barium peroxide.* Barium peroxide is made into a thin paste with ice-cold water and added slowly to an ice-cold dilute sulphuric acid. Barium sulphate thus precipitated is allowed to settle and filtered off when the filtrate obtained is a dilute solution of hydrogen peroxide. Hydrofluosilicic acid may be used in place of sulphuric acid.



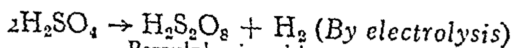
$$BaO_2+H_2SO_4 \rightarrow BaSO_4+H_2O_2$$

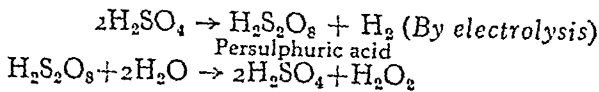
(*ii*) *By the action of carbon dioxide on barium peroxide.* Carbon dioxide is passed through barium peroxide paste in ice-cold water, as prepared above, in slow stream and the precipitate of barium carbonate so obtained is filtered off.



$$BaO_2+CO_2+H_2O \rightarrow BaCO_3+H_2O_2$$

(3) **Manufacture.** Hydrogen peroxide is being manufactured at present by the electrolysis of 50 per cent sulphuric acid followed by vacuum distillation. The distillate is 30 per cent solution of pure hydrogen peroxide.





$$2H_2SO_4 \rightarrow \underset{\text{Persulphuric acid}}{H_2S_2O_8} + H_2 \text{ (By electrolysis)}$$

$$H_2S_2O_8+2H_2O \rightarrow 2H_2SO_4+H_2O_2$$

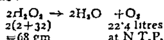
Concentration of Hydrogen Peroxide Solution. The dilute solution obtained in any of the above methods is concentrated :

(i) *By careful evaporation of the solution* obtained above on a water-bath preferably under reduced pressure and using a fractionating column. Hydrogen peroxide, being appreciably less volatile than water, loses water by evaporation till a 30 per cent solution is obtained. Since it results in concentration of impurities in the product and many of these impurities catalyse the decomposition, it is not advisable to concentrate it beyond about 33 per cent.

(ii) *By distillation under reduced pressure* at temperatures below 60°C the concentrates up to 90% solution of hydrogen peroxide can be obtained. At first water comes over, the receiver is changed to collect the later fraction containing hydrogen peroxide.

(iii) To get more concentrated solution and finally pure hydrogen peroxide, the 90% solution is cooled till crystallization sets in. The crystals are richer in hydrogen peroxide than the solution left behind. The crystals are separated, melted and refrozen to effect further concentration. Pure anhydrous hydrogen peroxide can be obtained by repeating this process.

give on heating 10 × 20 = 200 ml. of oxygen at N T P. Its percentage strength can be calculated as follows :



$$2H_2O_2 \rightarrow 2H_2O + O_2$$
$$2(2+32) \qquad 22{\cdot}4 \text{ litres}$$
$$=68 \text{ gm} \qquad \text{at N.T.P.}$$

From the chemical equation it is clear that 22·4 litres of oxygen at N.T.P. are obtained from 68 gm of H_2O_2

∵ 200 ml of oxygen at N.T P will be liberated by

$\frac{68}{22{,}400} \times 200 = 0{\cdot}607$ gm of H_2O_2 present in 10 ml. of the sample

∴ Strength of the 20 vol. hydrogen peroxide sample

$$= \frac{0{\cdot}607}{10} \times 1000 = 60{\cdot}7 \text{ gm /litre.}$$

22. **Physical Properties of Hydrogen Peroxide.**—It is a colourless, odourless, syrupy liquid (Sp. Gr. 1·46 and b.p. 85°C) in the anhydrous state. Bigger bulks are bluish in colour. It is miscible with water, alcohol and ether in all proportions.

23. **Chemical Properties.**—Chemical properties of hydrogen peroxide are discussed under four headings given below :

(a) **Decomposition.** Pure hydrogen peroxide is unstable and decomposes on standing or on heating when water and oxygen are formed.



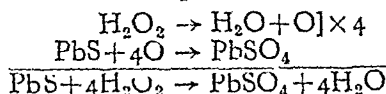
$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Presence of manganese dioxide, carbon or finely divided metals accelerates this decomposition. All of these substances are, therefore, called positive catalysts. Traces of acid, acetanilide or alcohol render it more stable, *i.e.*, serve as negative catalysts.

Dilute solutions (about 30%) of hydrogen peroxide keep fairly well in dark coloured bottles but decompose slowly when exposed to light.

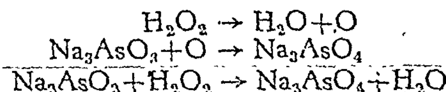
(*b*) **Oxidising Properties.** Due to its tendency to lose an atom of nascent oxygen, ($H_2O_2 \rightarrow H_2O+O$) it acts as a strong oxidising agent. For example—

(*i*) *It oxidises black lead sulphide to white lead sulphate.*



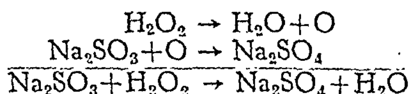
$$H_2O_2 \rightarrow H_2O+O] \times 4$$
$$PbS+4O \rightarrow PbSO_4$$
$$PbS+4H_2O_2 \rightarrow PbSO_4+4H_2O$$

(*ii*) *Arsenites are oxidised to arsenates.*



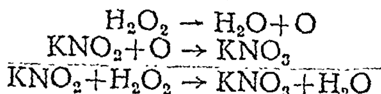
$$H_2O_2 \rightarrow H_2O+O$$
$$Na_3AsO_3+O \rightarrow Na_3AsO_4$$
$$Na_3AsO_3+H_2O_2 \rightarrow Na_3AsO_4+H_2O$$

(*iii*) *It oxidises sulphites to sulphates.*



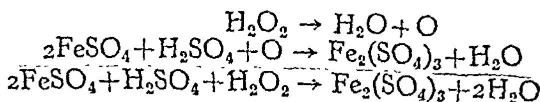
$$H_2O_2 \rightarrow H_2O+O$$
$$Na_2SO_3+O \rightarrow Na_2SO_4$$
$$Na_2SO_3+H_2O_2 \rightarrow Na_2SO_4+H_2O$$

(*iv*) *Nitrites are oxidised to nitrates.*



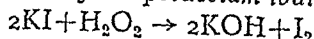
$$H_2O_2 \rightarrow H_2O+O$$
$$KNO_2+O \rightarrow KNO_3$$
$$KNO_2+H_2O_2 \rightarrow KNO_3+H_2O$$

(*v*) *Ferrous sulphate is oxidised to ferric sulphate.*



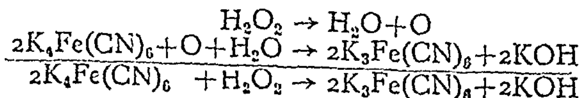
$$H_2O_2 \rightarrow H_2O+O$$
$$2FeSO_4+H_2SO_4+O \rightarrow Fe_2(SO_4)_3+H_2O$$
$$2FeSO_4+H_2SO_4+H_2O_2 \rightarrow Fe_2(SO_4)_3+2H_2O$$

(*vi*) *It liberates iodine from potassium iodide solution.*



$$2KI+H_2O_2 \rightarrow 2KOH+I_2$$

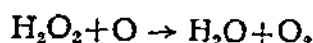
(*vii*) *An acidified solution of potassium ferrocyanide is oxidised to potassium ferricyanide.*



$$H_2O_2 \rightarrow H_2O+O$$
$$2K_4Fe(CN)_6+O+H_2O \rightarrow 2K_3Fe(CN)_6+2KOH$$
$$2K_4Fe(CN)_6+H_2O_2 \rightarrow 2K_3Fe(CN)_6+2KOH$$

Due to its oxidising property, it is a *valuable bleaching agent*, powerful but *harmless disinfectant and germicide.* Delicate materials like silk, wool, ivory, hair, which will be destroyed by chlorine, are bleached by hydrogen peroxide.

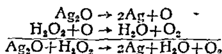
(*c*) **Reducing Properties.** Towards other oxidising agents it behaves as a reducing agent. This is due to the ease with which it can combine with an atom of oxygen.



$$H_2O_2 + O \rightarrow H_2O + O_2$$

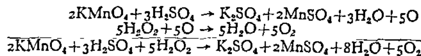
For example—

(*i*) *It reduces silver oxide to silver.*



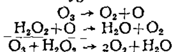
$$Ag_2O \rightarrow 2Ag + O$$
$$H_2O_2 + O \rightarrow H_2O + O_2$$
$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$$

(*ii*) *Potassium permanganate is decolorised to its reduction.*



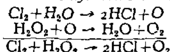
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$5H_2O_2 + 5O \rightarrow 5H_2O + 5O_2$$
$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(*iii*) *Ozone is reduced to oxygen.*



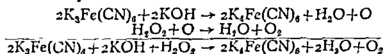
$$O_3 \rightarrow O_2 + O$$
$$H_2O_2 + O \rightarrow H_2O + O_2$$
$$O_3 + H_2O_2 \rightarrow 2O_2 + H_2O$$

(*iv*) *Chlorine is reduced to hydrochloric acid.*



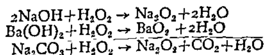
$$Cl_2 + H_2O \rightarrow 2HCl + O$$
$$H_2O_2 + O \rightarrow H_2O + O_2$$
$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$

(*v*) *Alkaline solution of potassium ferricyanide is reduced to potassium ferrocyanide.*



$$2K_3Fe(CN)_6 + 2KOH \rightarrow 2K_4Fe(CN)_6 + H_2O + O$$
$$H_2O_2 + O \rightarrow H_2O + O_2$$
$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 \rightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2$$

(*d*) **Acidic nature.** Hydrogen peroxide is slightly acidic in character though in dilute solution it is neutral towards litmus. It reacts with alkalis and carbonates to give their corresponding peroxides.



$$2NaOH + H_2O_2 \rightarrow Na_2O_2 + 2H_2O$$
$$Ba(OH)_2 + H_2O_2 \rightarrow BaO_2 + 2H_2O$$
$$Na_2CO_3 + H_2O_2 \rightarrow Na_2O_2 + CO_2 + H_2O$$

24. **Uses of Hydrogen Peroxide.**—Chief uses of hydrogen peroxide are :

(*i*) It destroys bacteria and finds use as an antiseptic and germicide for washing wounds, teeth and ears.

(*ii*) It destroys the colour of some organic compounds and is used in bleaching delicate things, *e.g.*, hair, wool, silk, ivory and feathers. With lower cost of production, hydrogen peroxide has become an important bleaching agent in textile mills.

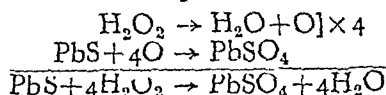
(*iii*) For restoring colour of lead paintings.

Presence of manganese dioxide, carbon or finely divided metals accelerates this decomposition. All of these substances are, therefore, called positive catalysts. Traces of acid, acetanilide or alcohol render it more stable, *i.e.*, serve as negative catalysts.

Dilute solutions (about 30%) of hydrogen peroxide keep fairly well in dark coloured bottles but decompose slowly when exposed to light.

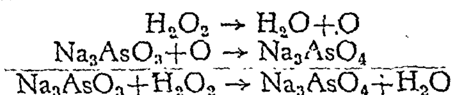
(*b*) **Oxidising Properties.** Due to its tendency to lose an atom of nascent oxygen, ($H_2O_2 \rightarrow H_2O+O$) it acts as a strong oxidising agent. For example—

(*i*) *It oxidises black lead sulphide to white lead sulphate.*



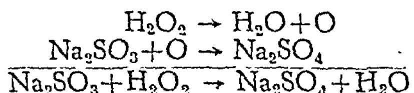
$$H_2O_2 \rightarrow H_2O+O] \times 4$$
$$PbS+4O \rightarrow PbSO_4$$
$$PbS+4H_2O_2 \rightarrow PbSO_4+4H_2O$$

(*ii*) *Arsenites are oxidised to arsenates.*



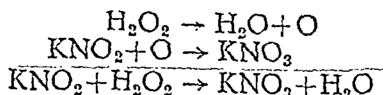
$$H_2O_2 \rightarrow H_2O+O$$
$$Na_3AsO_3+O \rightarrow Na_3AsO_4$$
$$Na_3AsO_3+H_2O_2 \rightarrow Na_3AsO_4+H_2O$$

(*iii*) *It oxidises sulphites to sulphates.*



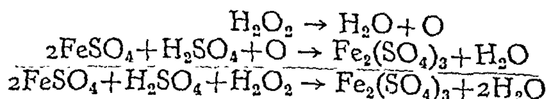
$$H_2O_2 \rightarrow H_2O+O$$
$$Na_2SO_3+O \rightarrow Na_2SO_4$$
$$Na_2SO_3+H_2O_2 \rightarrow Na_2SO_4+H_2O$$

(*iv*) *Nitrites are oxidised to nitrates.*



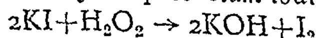
$$H_2O_2 \rightarrow H_2O+O$$
$$KNO_2+O \rightarrow KNO_3$$
$$KNO_2+H_2O_2 \rightarrow KNO_3+H_2O$$

(*v*) *Ferrous sulphate is oxidised to ferric sulphate.*



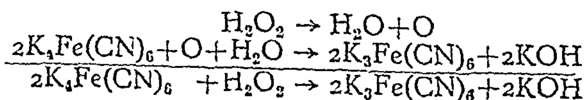
$$H_2O_2 \rightarrow H_2O+O$$
$$2FeSO_4+H_2SO_4+O \rightarrow Fe_2(SO_4)_3+H_2O$$
$$2FeSO_4+H_2SO_4+H_2O_2 \rightarrow Fe_2(SO_4)_3+2H_2O$$

(*vi*) *It liberates iodine from potassium iodide solution.*



$$2KI+H_2O_2 \rightarrow 2KOH+I_2$$

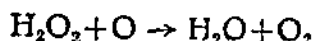
(*vii*) *An acidified solution of potassium ferrocyanide is oxidised to potassium ferricyanide.*



$$H_2O_2 \rightarrow H_2O+O$$
$$2K_4Fe(CN)_6+O+H_2O \rightarrow 2K_3Fe(CN)_6+2KOH$$
$$2K_4Fe(CN)_6+H_2O_2 \rightarrow 2K_3Fe(CN)_6+2KOH$$

Due to its oxidising property, it is a *valuable bleaching agent,* powerful but *harmless disinfectant and germicide.* Delicate materials like silk, wool, ivory, hair, which will be destroyed by chlorine, are bleached by hydrogen peroxide.

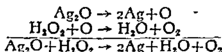
(c) **Reducing Properties.** Towards other oxidising agents it behaves as a reducing agent. This is due to the ease with which it can combine with an atom of oxygen.



$$H_2O_2 + O \rightarrow H_2O + O_2$$

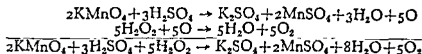
For example—

(i) *It reduces silver oxide to silver.*



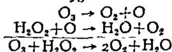
$$\begin{array}{l} Ag_2O \rightarrow 2Ag + O \\ H_2O_2 + O \rightarrow H_2O + O_2 \\ \hline Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2 \end{array}$$

(ii) *Potassium permanganate is decolorised to its reduction.*



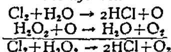
$$\begin{array}{l} 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O \\ 5H_2O_2 + 5O \rightarrow 5H_2O + 5O_2 \\ \hline 2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2 \end{array}$$

(iii) *Ozone is reduced to oxygen.*



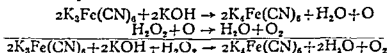
$$\begin{array}{l} O_3 \rightarrow O_2 + O \\ H_2O_2 + O \rightarrow H_2O + O_2 \\ \hline O_3 + H_2O_2 \rightarrow 2O_2 + H_2O \end{array}$$

(iv) *Chlorine is reduced to hydrochloric acid.*



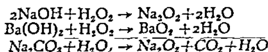
$$\begin{array}{l} Cl_2 + H_2O \rightarrow 2HCl + O \\ H_2O_2 + O \rightarrow H_2O + O_2 \\ \hline Cl_2 + H_2O_2 \rightarrow 2HCl + O_2 \end{array}$$

(v) *Alkaline solution of potassium ferricyanide is reduced to potassium ferrocyanide.*



$$\begin{array}{l} 2K_3Fe(CN)_6 + 2KOH \rightarrow 2K_4Fe(CN)_6 + H_2O + O \\ H_2O_2 + O \rightarrow H_2O + O_2 \\ \hline 2K_3Fe(CN)_6 + 2KOH + H_2O_2 \rightarrow 2K_4Fe(CN)_6 + 2H_2O + O_2 \end{array}$$

(d) **Acidic nature.** Hydrogen peroxide is slightly acidic in character though in dilute solution it is neutral towards litmus. It reacts with alkalis and carbonates to give their corresponding peroxides.



$$\begin{array}{l} 2NaOH + H_2O_2 \rightarrow Na_2O_2 + 2H_2O \\ Ba(OH)_2 + H_2O_2 \rightarrow BaO_2 + 2H_2O \\ Na_2CO_3 + H_2O_2 \rightarrow Na_2O_2 + CO_2 + H_2O \end{array}$$

24. **Uses of Hydrogen Peroxide.**—Chief uses of hydrogen peroxide are :

(i) It destroys bacteria and finds use as an antiseptic and germicide for washing wounds, teeth and ears.

(ii) It destroys the colour of some organic compounds and is used in bleaching delicate things, *e.g.*, hair, wool, silk, ivory and feathers. With lower cost of production, hydrogen peroxide has become an important bleaching agent in textile mills.

(iii) For restoring colour of lead paintings.

(*iv*) As an oxidising agent in the laboratory.

(*v*) As a source of oxygen for rockets.

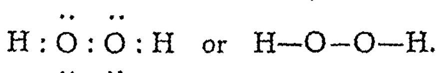
25. **Tests for Hydrogen Peroxide.**—(*i*) It decolorises acidified potassium permanganate solution.

(*ii*) It turns starch iodide paper blue.

(*iii*) When shaken with potassium dichromate solution in sulphuric acid and ether, a beautiful blue colour is seen in the ethereal layer.

(*iv*) With a solution of titanium oxide (TiO_2) it gives orange colour.

26. **Structure of Hydrogen Peroxide.**—Molecular formula of hydrogen peroxide is H_2O_2. Its electronic formula is



$$H:\ddot{\underset{..}{O}}:\ddot{\underset{..}{O}}:H \quad \text{or} \quad H—O—O—H.$$

To understand its structure consider a book opened at an angle of 90°. The two oxygen atoms may be pictured as lying on the spine of the book while the two hydrogen atoms are placed one on each cover with H—O—O bond angle = 101·5° (Fig. 30·13). An orbital diagram of H_2O_2 is shown in Fig. 30·14.

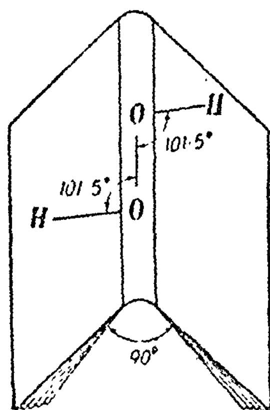


Fig. 30·13—Structure of hydrogen peroxide.

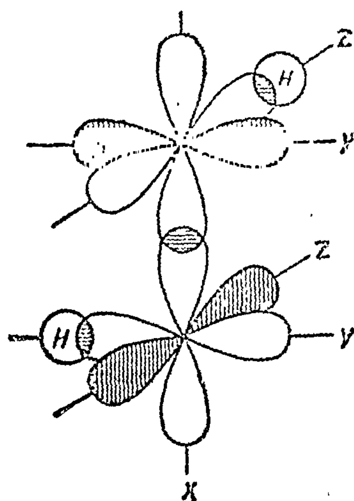


Fig. 30·14—An orbital diagram of H_2O_2 (vertical shading indicates lone pair ; horizontal shading shows overlap regions).

27. Distinction between Hydrogen Peroxide and Ozone.—We can distinguish between hydrogen peroxide and ozone by studying their properties as given in the table below :

Property	Ozone	Hydrogen peroxide
1. State	Pale blue gas	Colourless
2. Odour	Characteristic	Odourless
3. Action on		
(i) Mercury	"tailing"	No action
(ii) Benzidine paper	Turned brown	,, ,,
(iii) Tetramethyl base paper	,, violet	,, ,,
4. Starch iodide paper	Turned blue but no action in presence of $FeSO_4$	Turned blue even in presence of $FeSO_4$.
5. Action on		
(i) Acidified $KMnO_4$	No action	Decolorised
(ii) Acidified $K_2Cr_2O_7$ and ether	,, ,,	Blue colour in ethereal layer.
(iii) TiO_2 soln.	,, ,,	Turned orange.
(iv) Ag_2O soln.	,, ,,	Reduced to silver.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Water+(i) Calcium hydride, (ii) Aluminium nitride, (iii) Calcium phosphide, (iv) Calcium carbide.

2. Magnesium or Calcium bicarbonate heated or treated with (i) Lime (ii) Washing soda, (iii) Caustic soda, (iv) Permutit.

3. Dilute sulphuric acid+(i) Sodium peroxide, (ii) Barium peroxide paste.

4. Barium peroxide paste+Carbon dioxide.

5. Hydrogen peroxide+(i) Lead sulphide, (ii) Sodium arsenite, (iii) [illegible] ...assium [illegible] Chlo- [illegible] bonate, [illegible] potas-

QUESTIONS

Essay-type Questions

1. What are the different sources of natural waters ? How would you purify water in the laboratory and on a large scale ?
What is meant by free and combined water ? How can you detect small traces of water ? What is the action of steam on (a) coke, and (b) iron ?

2. Describe briefly the methods of purifying the drinking water of a large city. Is hard water always unfit for drinking ? Is soft water always good for drinking ?

3. What are the substances that make water hard ? Why does the hardness of water render it unfit for use in boilers and for washing purposes ? How can hard water be rendered suitable for the above uses ?
(Delhi H S. 1972, 71, 70, 69 , All-India H S 1959, 67, 65)

4. (a) What do you understand by the hardness in water ? How can the permanent and temporary hardness be determined in a sample of water ?
Discuss the modern methods used for purification of water ?
(Delhi Pre-Medical 1951)
(b) How is chemically pure water prepared ? *(Nagpur Pre-Univ [illegible])*

5. How is water made fit for drinking purposes? Why is hard water not economical for washing purposes? Why is sea water not used for generating steam in boilers? *(Punjab Pre-University 1964; Nagpur 1970)*

6. (*a*) Describe a synthetic method of determining the composition of water by volume.

(*b*) Describe Morley's experiment for the determination of the composition of water by weight.

7. Describe the preparation of pure hydrogen peroxide. Illustrate the use of this compound as an oxidising agent and as a reducing agent. Mention its important uses. What do you understand by 30 volume hydrogen peroxide.
(Delhi Pre-Medical 1961; All-India H.S. 1969; Delhi H.S. 1969, 67; U.P. Board Inter. 1969; Punjab Pre-Univ. 1969)

8. How would you prepare hydrogen peroxide in the laboratory? What is the most effective method of concentrating a 50% sample of hydrogen peroxide?

Give chemical equations showing the action of hydrogen peroxide on— (*i*) Lead sulphide; (*ii*) Silver oxide; (*iii*) Sodium carbonate; (*iv*) Potassium iodide; (*v*) Ferrous sulphate; and (*vi*) Potassium permanganate.
(Nagpur Pre-Univ. 1970; Delhi H.S. 1970, 66, 65)

9. How is hydrogen peroxide prepared? Describe its properties and uses. Compare in a tabular form its properties with those of ozone. Explain giving equations how hydrogen peroxide reacts with ferrous sulphate, lead sulphide, chlorine and acidified potassium permanganate? *(All India H.S. 1967)*

10. (*a*) Give the preparation, properties and uses of hydrogen peroxide.
(Punjab Pre-University 1964; U.P. Board Inter. 1963)

(*b*) How is hydrogen peroxide prepared on a large scale? Give three reactions in which it acts as an oxidising agent, three reactions in which it acts as a reducing agent and one in which it acts as an acid.
(Punjab Pre-University 1969; U.P. Board Inter. 1971)

11. What volume of oxygen at N.T.P. will be evolved by the decomposition of 100 c.c. of a hydrogen peroxide solution marked 30 volumes?
[Ans. 3,000 c.c.]

Test Your Understanding

12. Fill in the blanks in the following:

(*i*) Temporary hard water contains...........while permanent hard water contains.........of.........

(*ii*) Chemically permutit is.........and calgon is the trade name of.........

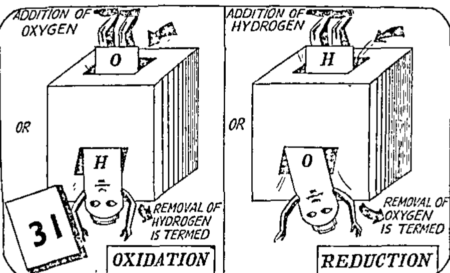
(*iii*) Ion exchange resin consists of.........arranged in the form of........... having......or......groups.

(*iv*) Hydrogen peroxide is prepared by the action of.........on sodium peroxide or by the action of......,...or......on barium peroxide.

(*v*) It is manufactured by electrolysis of......followed by.........

KEY

(i) bicarbonates, sulphates and chlorides, calcium, magnesium and iron; (ii) Sodium aluminium silicate, sodium hexametaphosphate; (*iii*) giant organic molecules, porous framework, COOH, OH; (*iv*) Ice-cold dilute H_2SO_4, Ice-cold dil. H_2SO_4, H_3PO_4, CO_2; (*v*) 50%H_2SO_4, vacuum distillation.



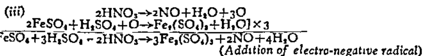
Oxidation and Reduction

1. **Oxidation.**—Oxidation has already been defined as a process of combination of an element with oxygen. This definition is, however, too limited for most purposes. The scope of the term has, therefore, been much widened. At present *oxidation is any process involving addition of oxygen or any other electro-negative*

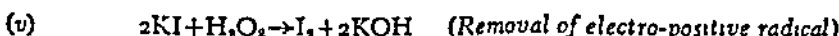
of hydrogen or any other


(i) $C + O_2 \rightarrow CO_2$ *(Addition of oxygen)*


(ii) $2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$ *(Addition of electro-negative radical)*


(iii)
$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$
$$[2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$
$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$
(Addition of electro-negative radical)


(iv) $H_2S + Cl_2 \rightarrow S + 2HCl$ *(Removal of hydrogen)*

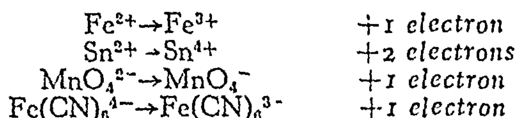

(v) $2KI + H_2O_2 \rightarrow I_2 + 2KOH$ *(Removal of electro-positive radical)*

are all cases of oxidation.

2. **Oxidation involves loss of Electrons**—When an element combines with oxygen, it loses electrons which are transferred to oxygen. This fact has been generalised and now *oxidation is any reaction in which an atom or ion loses electrons.* For this reason *oxidation is usually referred to as De-electronation.*

For example, when mercury atoms form mercurous ions they lose electrons. They are said to be oxidised. Further when these mercurous ions form mercuric ions, they lose more electrons. They are said to have been further oxidised. Similarly iodide ions in

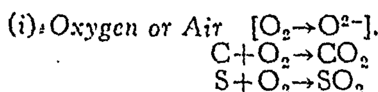
becoming iodine atoms lose electrons and are said to have been oxidised. Change of ferrous (Fe^{2+}) to ferric (Fe^{3+}), stannous (Sn^{2+}) to stannic (Sn^{4+}), manganate (MnO_4^{2-}) to permanganate (MnO_4^-) and ferrocyanide $[Fe(CN)_6]^{4-}$ to ferricyanide $[Fe(CN)_6]^{3-}$ are all cases of oxidation, as each one of them involves a loss of electrons.



$$Fe^{2+} \rightarrow Fe^{3+} + 1 \textit{ electron}$$
$$Sn^{2+} \rightarrow Sn^{4+} + 2 \textit{ electrons}$$
$$MnO_4^{2-} \rightarrow MnO_4^- + 1 \textit{ electron}$$
$$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + 1 \textit{ electron}$$

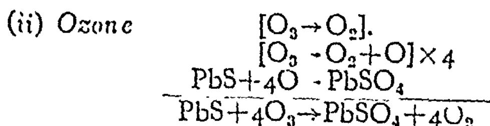
It is interesting to note in the above examples that oxidation results in an increase in positive valency or a decrease in negative valency. *Hence oxidation can also be defined as a process involving increase in positive valency or decrease in negative valency.*

3. **Oxidising Agents.**—*Substances, which are capable of giving oxygen to other substances or contain an atom or group of atoms which readily gains electrons, are called oxidising agents.* For example, during oxidation of lead to lead oxide, oxygen is supplied by air. In this case air is the oxidising agent. Some important oxidising agents and their common reduction products are :



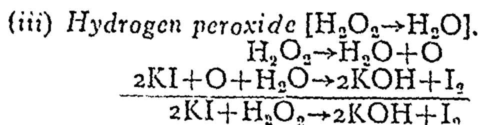
(i) *Oxygen or Air* $[O_2 \rightarrow O^{2-}]$.

$$C + O_2 \rightarrow CO_2$$
$$S + O_2 \rightarrow SO_2$$



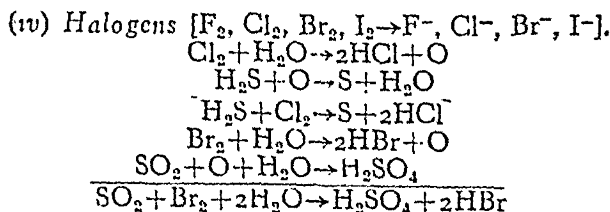
(ii) *Ozone* $[O_3 \rightarrow O_2]$.

$$[O_3 \rightarrow O_2 + O] \times 4$$
$$PbS + 4O \rightarrow PbSO_4$$
$$\overline{PbS + 4O_3 \rightarrow PbSO_4 + 4O_2}$$



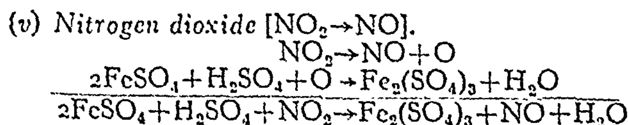
(iii) *Hydrogen peroxide* $[H_2O_2 \rightarrow H_2O]$.

$$H_2O_2 \rightarrow H_2O + O$$
$$2KI + O + H_2O \rightarrow 2KOH + I_2$$
$$\overline{2KI + H_2O_2 \rightarrow 2KOH + I_2}$$



(iv) *Halogens* $[F_2, Cl_2, Br_2, I_2 \rightarrow F^-, Cl^-, Br^-, I^-]$.

$$Cl_2 + H_2O \rightarrow 2HCl + O$$
$$H_2S + O \rightarrow S + H_2O$$
$$\overline{H_2S + Cl_2 \rightarrow S + 2HCl}$$
$$Br_2 + H_2O \rightarrow 2HBr + O$$
$$SO_2 + O + H_2O \rightarrow H_2SO_4$$
$$\overline{SO_2 + Br_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr}$$

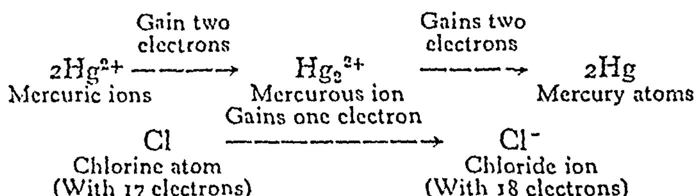


(v) *Nitrogen dioxide* $[NO_2 \rightarrow NO]$.

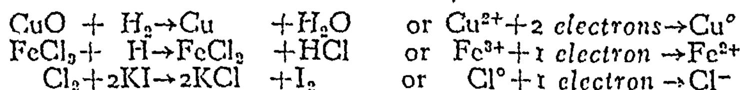
$$NO_2 \rightarrow NO + O$$
$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$$
$$\overline{2FeSO_4 + H_2SO_4 + NO_2 \rightarrow Fe_2(SO_4)_3 + NO + H_2O}$$

5. **Reduction involves gain of Electrons.**—Elements losing oxygen during reduction gain back their electrons. Chemists define *reduction as any reaction in which an atom or ion gains electrons.* For this reason *reduction is often referred to as* **Electronation.**

For example, formation of mercurous ions from mercuric ions or the formation of mercury atoms from mercurous or mercuric ions are all reduction processes. Likewise formation of chloride ion from chlorine atoms is reduction.



In terms of valency change **reduction** *involves a decrease in positive valency or an increase in negative valency, e.g.,*

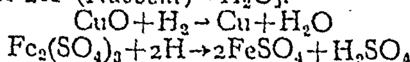


$$CuO + H_2 \rightarrow Cu + H_2O \quad \text{or} \quad Cu^{2+} + 2\ \textit{electrons} \rightarrow Cu^{\circ}$$
$$FeCl_3 + H \rightarrow FeCl_2 + HCl \quad \text{or} \quad Fe^{3+} + 1\ \textit{electron} \rightarrow Fe^{2+}$$
$$Cl_2 + 2KI \rightarrow 2KCl + I_2 \quad \text{or} \quad Cl^{\circ} + 1\ \textit{electron} \rightarrow Cl^-$$

Similarly in (*v*) above $[Fe(CN)_6]^{3-} + 1\ \textit{electron} \rightarrow [Fe(CN)_6]^{4-}$.

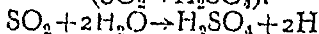
6. **Reducing Agents.**—*A substance which brings about reduction by supplying electrons is called a* **reducing agent.** Some important reducing agents and their common oxidation products are listed below :

(*i*) *Hydrogen* [H_2 or 2H (*Nascent*) $\rightarrow H_2O$].

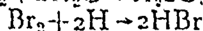


$$CuO + H_2 \rightarrow Cu + H_2O$$
$$Fe_2(SO_4)_3 + 2H \rightarrow 2FeSO_4 + H_2SO_4$$

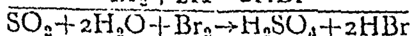
(*ii*) *Sulphur dioxide* ($SO_2 \rightarrow H_2SO_4$).



$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$

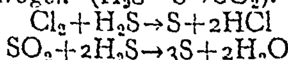


$$Br_2 + 2H \rightarrow 2HBr$$



$$SO_2 + 2H_2O + Br_2 \rightarrow H_2SO_4 + 2HBr$$

(*iii*) *Sulphuretted hydrogen* ($H_2S \rightarrow S \rightarrow SO_2$).

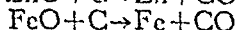


$$Cl_2 + H_2S \rightarrow S + 2HCl$$
$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

(*iv*) *Carbon* ($C \rightarrow CO \rightarrow CO_2$).

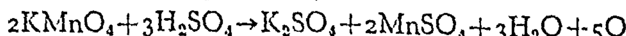


$$ZnO + C \rightarrow Zn + CO$$

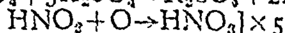


$$FeO + C \rightarrow Fe + CO$$

(*v*) *Nitrous acid* ($HNO_2 \rightarrow HNO_3$).



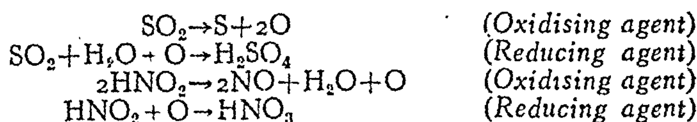
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$



$$HNO_2 + O \rightarrow HNO_3] \times 5$$



$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$



$SO_2 \rightarrow S + 2O$ *(Oxidising agent)*

$SO_2 + H_2O + O \rightarrow H_2SO_4$ *(Reducing agent)*

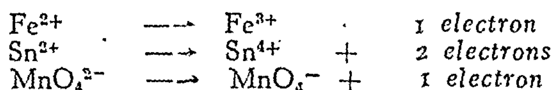
$2HNO_2 \rightarrow 2NO + H_2O + O$ *(Oxidising agent)*

$HNO_2 + O \rightarrow HNO_3$ *(Reducing agent)*

SOME MODERN CONCEPTS

8. **Oxidation Numbers.**– Oxidation is any reaction in which an atom or ion loses electrons. On the other hand, reduction is defined as any reaction in which an atom or ion gains electrons. As oxidation involves removal of electrons it has also been termed *de-electronation*. Similarly reduction may be referred to as *electronation*.

Change of ferrous (Fe^{2+}) to ferric (Fe^{3+}), stannous (Sn^{2+}) to stannic (Sn^{4+}), manganate (MnO_4^{2-}) to permanganate (MnO_4^-) are all cases of oxidation as each one of them involves a loss of electrons.

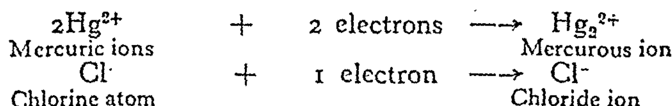


$Fe^{2+} \longrightarrow Fe^{3+}$ · *1 electron*

$Sn^{2+} \longrightarrow Sn^{4+} +$ *2 electrons*

$MnO_4^{2-} \longrightarrow MnO_4^- +$ *1 electron*

Similarly formation of mercurous ions (Hg_2^{2+}) from mercuric ions (Hg^{2+}) and formation of chloride ions (Cl^-) from chlorine atoms are cases of reduction as both involve a gain of electrons.



$2Hg^{2+}$ (Mercuric ions) + 2 electrons $\longrightarrow Hg_2^{2+}$ (Mercurous ion)

$Cl^{\cdot}$ (Chlorine atom) + 1 electron $\longrightarrow Cl^-$ (Chloride ion)

In order to keep track of electron shifts in oxidation-reduction reactions, it is convenient to use the concept of oxidation number or oxidation state of various atoms involved in oxidation-reduction reactions. *The oxidation number is defined as the charge which an atom appears to have when electrons are counted* in accordance with the following rather arbitrary rules :

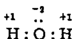
(*a*) *Electrons shared between two unlike atoms are counted with more electronegative atom.* For example, the electron pair



shared between H and Cl in $\overset{+1}{H} : \overset{-1}{\ddot{\underset{\cdot\cdot}{Cl}}} :$ is counted with more electronegative Cl. As a result of it hydrogen having lost share in the electron pair appears to have +1 charge and chlorine appears to have −1 charge. Hence oxidation numbers of H and Cl are +1 and −1 respectively.

(*b*) *Electrons shared between two like atoms are divided equally between the two sharing atoms.* For example, in hydrogen molecule H : H, the electron pair is equally shared between the two atoms. Thus both the atoms appear to have no charge, *i.e.*, oxidation number of hydrogen is 0 in hydrogen molecule.

In the molecule of water given in the margin, the two electron pairs shared between oxygen and the two hydrogen atoms are counted with the more electronegative oxygen atom. Hence in water oxidation number of each H is +1 and that of the O-atom is −2.



Water Molecule

Counting of electrons like this is very laborious. The following operational rules derived from the above will be found very convenient :

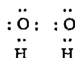
(1) In the element or uncombined state, the atoms are assigned an oxidation number of zero.

(2) In compounds, the oxidation number of fluorine is always −1.

(3) In compounds, the group I elements (Li, Na, K, Rb, Cs and Fr) have an oxidation number +1 and the group II elements (Be, Mg, Ca, Sr, Ba and Ra) have an oxidation number +2.

(4) Oxidation number of hydrogen in compounds is generally +1 except in metallic hydrides wherein its oxidation number is −1.

(5) In compounds, the oxidation number of oxygen is generally −2 except in F_2O wherein oxidation number of fluorine is −1 and that of oxygen is +2. In hydrogen peroxide molecule, the electron pair shared between O and H is counted with O but the other electron pair shared between two O=atoms is equally shared. The number of electrons counted with each O is, therefore, seven (i.e., one more than its own electrons). The oxygen atom, therefore, appears to have −1 charge or its oxidation number in H_2O_2 is −1.



Hydrogen peroxide

(6) In neutral molecules, the sum of the oxidation numbers of all the atoms is zero.

(7) For complex ions (charged species), the sum of the oxidation numbers of all the atoms is equal to the net charge on the ion.

With the help of these operational rules, we can calculate the oxidation number of an atom present in molecule or complex ion as illustrated in the following examples :

Example 1. *What is the oxidation number of S in (a) H_2SO_4, (b) $H_2S_2O_7$, and (c) $Na_2S_2O_3$?*

(a) Let oxidation number of S be x.

Sum of oxidation numbers of various atoms in H_2SO_4

$$=2\times(+1)+x+4\times(-2)$$
$$=2+x-8=x-6$$

This sum must be zero (rule 6). Hence

$$x-6=0$$

whence $x=6$

or oxidation number of various atoms in $H_2SO_4=+6$.

(*b*) Sum of oxidation numbers of various atoms in $H_2S_2O_7$

$$=2\times(+1)+2x+7\times(-2)$$
$$=2+2x-14=2x-12$$

Putting

$2x-12=0$ as above, we have

$$x=+6$$

∴ Oxidation number of S in $H_2S_2O_7=+6$.

(*c*) Sum of oxidation numbers of various atoms in $Na_2S_2O_3$

$$=2\times(+1)+2x+3\times(-2)$$
$$=2+2x-6=2x-4$$

Putting

$2x-4=0$, we have

$$x=+2$$

∴ Oxidation number of S in $Na_2S_2O_3=+2$.

Example 2. *What is the oxidation number of Mn in (a) MnO, (b) $KMnO_4$, and (c) K_2MnO_4 ?*

(*a*) Let the oxidation number of Mn be x. Sum of the oxidation numbers of various atoms in $MnO=x-2$.

Putting $x-2=0$, we have

$$x=+2$$

∴ Oxidation number of Mn in MnO is $+2$.

(*b*) Sum of oxidation numbers of various atoms in $KMnO_4$

$$=1+x+4\times(-2)=1+x-8$$
$$=x-7$$

Putting $x-7=0$, we get

$$x=+7$$

∴ Oxidation number of Mn in $KMnO_4$ is $+7$.

(*c*) Sum of oxidation numbers of various atoms in K_2MnO_4

$$=2\times(+1)+x+4\times(-2)$$
$$=2+x-8=x-6$$

Putting $x-6=0$, we get

$$x=+6$$

∴ Oxidation number of Mn in $K_2MnO_4=+6$.

Example 3. *What is the oxidation number of Cr or $Cr_2O_7^{2-}$?*

Let the oxidation number of Cr be x. Sum of oxidation numbers$=2x+7\times(-2)=-2$ (charge of the ion)

or $2x-14=-2$

whence $x=+6$

∴ Oxidation number of Cr in $Cr_2O_7^{2-}$ is $+6$.

For shorthand convenience, oxidation numbers of various atoms and their apparent contribution to charge is written below the atoms themselves. The sum is equated to zero or actual charge of the ion to calculate x. After a little practice these calculations are done mentally. For example, in finding the oxidation number of P($=x$ say) in

H_2	P_2	O_7^{2-}	
$+1$	x	-2	←*Oxidation numbers*
$+2$	$+2x$	-14	←*Apparent charge contribution*

Equating the apparent charge contribution to charge of the ion ($=-2$), we have

$$2x-12=-2$$

whence $x=+5$.

EXERCISE

1. Calculate the oxidation number of P in PH_4^+, $H_2PO_2^-$, PO_4^{3-} and HPO_3^{2-}. [Ans. -3 ; $+1$; $+5$; $+3$.

2. Calculate the oxidation number of C in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4. [Ans. -4 ; -2 ; 0 ; $+2$; $+4$.

3. Calculate the oxidation number of S in $Na_2S_4O_6$. [Ans. $+10/4$.

4. Calculate the oxidation number of C in $C_{12}H_{22}O_{11}$. [Ans. 0.

9. Valency, Oxidation State and Oxidation Number.—

Valency of an element is defined as a *number* indicating its combining capacity. For example, it represents the number of hydrogen atoms which can combine with a given atom. It also represents the number of single bonds which an atom can form. It is also defined as a number of electrons its atom is able to lend, borrow or share. *In any case valency is a pure number and has no plus or minus sign associated with it.*

Oxidation number is defined as the charge which an atom appears to have when electrons are counted. *It is positive or negative.* For example, in ammonia the valency of nitrogen is three but its oxidation number is -3.

In ionic compounds the oxidation state of an element is the same as the charge on the ion formed from an atom of the element. For example, in potassium bromide potassium is said to be in the $+1$ oxidation state and bromine in -1 oxidation state. It ionizes as

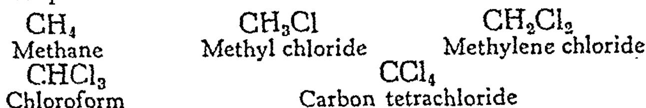


$$KBr \rightleftharpoons K^+ + Br^-$$

In other words, oxidation numbers of potassium and bromine are $+1$ and -1 respectively.

Oxidation state of aluminium in Al_2O_3 is $+3$ and the total oxidation number of two aluminium atoms is $+6$. Thus *oxidation state of an element is its oxidation number per atom.*

There may actually be a difference between the magnitude of valency and the oxidation number. For example, consider the following compounds of carbon :



CH_4 Methane CH_3Cl Methyl chloride CH_2Cl_2 Methylene chloride

$CHCl_3$ Chloroform CCl_4 Carbon tetrachloride

In each case one atom of carbon shares a total of 4 pairs of electrons with other atoms. Carbon atom is, therefore, tetravalent in each case.

Oxidation number for carbon in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 is -4, -2, 0, $+2$ and $+4$ respectively.

Thus while valency of carbon remains constant (=4) in each one of the five compounds, its oxidation number varies from -4 to $+4$.

10. Oxidation and Reduction in terms of Oxidation Numbers.—The term **oxidation** *refers to any chemical change involving increase in oxidation number* whereas the term **reduction** *applies to any chemical change involving decrease in oxidation number.*

Consider the following chemical changes :



(*i*) $2H_2 + O_2 \rightarrow 2H_2O$

Herein oxidation number of hydrogen changes from 0 (in H_2) to $+1$ (in H_2O). It is, therefore, a case of oxidation of hydrogen.

(*ii*) Sugar ($C_{12}H_{22}O_{11}$) burns to give CO_2 and water. In this oxidation number of carbon increases from 0 (in $C_{12}H_{22}O_{11}$) to $+4$ in CO_2. The sugar is, therefore, said to have undergone oxidation.

(*iii*) When oxygen reacts with hydrogen to give water [example (*i*)] the oxidation number of oxygen decreases from 0 (in O_2) to -2 (in H_2O). It is, therefore, a case of reduction of oxygen.

In the same reaction, oxidation number of hydrogen increases, and that of oxygen decreases, *i.e.*, hydrogen undergoes oxidation while oxygen undergoes reduction. Thus oxidation and reduction occur together. This is because in oxidation and reduction change of oxidation number occurs as a result of the shift of electrons from one atom *A* to the other atom *B* which pulls the electrons towards it. As a result of this electron shift oxidation number of *A* increases and that of *B* decreases. Oxidation and reduction must, therefore, always occur together.

An oxidising agent is a substance which brings about oxidation. It contains an atom which undergoes a decrease in oxidation number. It can also be defined as a substance which picks up electrons and thus brings about de-electronation.

Potassium chlorate ($KClO_3$) is an oxidising agent and during the reaction it is converted to KCl. In this oxidation number of Cl decreases from $+5$ (in $KClO_3$) to -1 (in KCl). This amounts to its picking up of six electrons from other atoms.

A ... tion.
It conta ... ber.
It may ...

Sulphurous acid (H_2SO_3) is a reducing agent and during the reaction in ... oxidised to sulphuric ... number of S increas ...

Various terms used in oxidation-reduction are summarised in the following table :

Term	Oxidation number change	Electron change
Oxidation	Increases	Loss of electrons
Reduction	Decreases	Gain of electrons
Oxidising agent	Decreases	Picks up electrons
Reducing agent	Increases	Supplies electrons

11. **The Activity Series.**—While discussing the preparation and properties of hydrogen and oxygen we noticed that—

(i) Some metals displace hydrogen from water at room temperature.

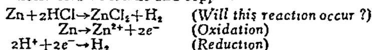
(ii) A number of metals displace hydrogen from acids.

(iii) Some metals burn brilliantly in oxygen while others do not.

On the basis of these differences in chemical activity, the ...

metals in such activity series or electrochemical series.

In this series element at the top has the greatest tendency to give up ele... the least. ... occur or n... : ... dilute hydrochloric acid with zinc and copper.

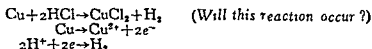


$Zn+2HCl \rightarrow ZnCl_2+H_2$ (*Will this reaction occur ?*)

$Zn \rightarrow Zn^{2+}+2e^-$ (*Oxidation*)

$2H^+ + 2e^- \rightarrow H_2$ (*Reduction*)

Zinc being above hydrogen in the activity series is expected to lose electrons readily to hydrogen ion. Hence the reaction will occur.



$Cu+2HCl \rightarrow CuCl_2+H_2$ (*Will this reaction occur ?*)

$Cu \rightarrow Cu^{2+}+2e^-$

$2H^+ + 2e \rightarrow H_2$

Table 31·1—Activity Series of Metals

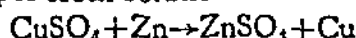
When heated	Metal	Typical reactions			
	"Base" end				
Not reduced by hydrogen	Li	React with cold water	React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	K	React with cold water	React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Na	React with cold water	React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Ba	React with cold water	React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Sr	React with cold water	React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Ca	React with cold water	React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Mg		React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Al		React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Mn		React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Zn		React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Not reduced by hydrogen	Cr		React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Reduced by hydrogen	Fe		React with steam	React with acids, liberating hydrogen	React with oxygen, giving oxides
Reduced by hydrogen	Co			React with acids, liberating hydrogen	React with oxygen, giving oxides
Reduced by hydrogen	Ni			React with acids, liberating hydrogen	React with oxygen, giving oxides
Reduced by hydrogen	Sn			React with acids, liberating hydrogen	React with oxygen, giving oxides
Reduced by hydrogen	Pb			React with acids, liberating hydrogen	React with oxygen, giving oxides
Reduced by hydrogen	Hydrogen				React with oxygen, giving oxides
Reduced by hydrogen	Cu				React with oxygen, giving oxides
Reduced by heat alone	Hg				React with oxygen, giving oxides
Reduced by heat alone	Ag				Form oxides indirectly
Reduced by heat alone	Pt				Form oxides indirectly
Reduced by heat alone	Au				Form oxides indirectly
	"Noble" end				

In this case copper being below hydrogen in the activity series is not expected to lose electrons to hydrogen ions. Hence this reaction will not occur.

In general—

(i) Metals placed above hydrogen liberate hydrogen from acids.

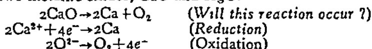
(ii) Metals higher up in the series will displace those below which are less active from their solutions. For example, zinc displaces copper from solution.



$$CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$$

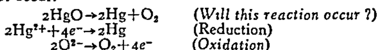
(iii) Only very active metals react with water at room temperature. The reduction of H_2O is more difficult than reduction of H^+ ions.

Now let us consider the possibility of preparing oxygen by heating the two metallic oxides, CaO and HgO.



$$2CaO \rightarrow 2Ca + O_2 \quad \text{(Will this reaction occur ?)}$$
$$2Ca^{2+} + 4e^- \rightarrow 2Ca \quad \text{(Reduction)}$$
$$2O^{2-} \rightarrow O_2 + 4e^- \quad \text{(Oxidation)}$$

Calcium is towards the top of the activity series. Ca^{2+} ions are, therefore, difficult to reduce. We should expect that the reaction will not occur.



$$2HgO \rightarrow 2Hg + O_2 \quad \text{(Will this reaction occur ?)}$$
$$2Hg^{2+} + 4e^- \rightarrow 2Hg \quad \text{(Reduction)}$$
$$2O^{2-} \rightarrow O_2 + 4e^- \quad \text{(Oxidation)}$$

Mercury being towards the bottom of the activity series loses electrons with difficulty and would, therefore, gain electrons readily. We would, therefore, expect this reaction to occur. Mercuric oxide decomposes on heating and gives oxygen.

In general—

(i) Metals lying above hydrogen rust easily, those below it do not.

(ii) Oxides of manganese and other metals above it cannot be reduced to the metallic state by heating in a current of hydrogen.

(iii) Oxides of iron and other metals below it can be easily reduced.

(iv) Oxides of mercury and the metals lying below it, decompose when heated.

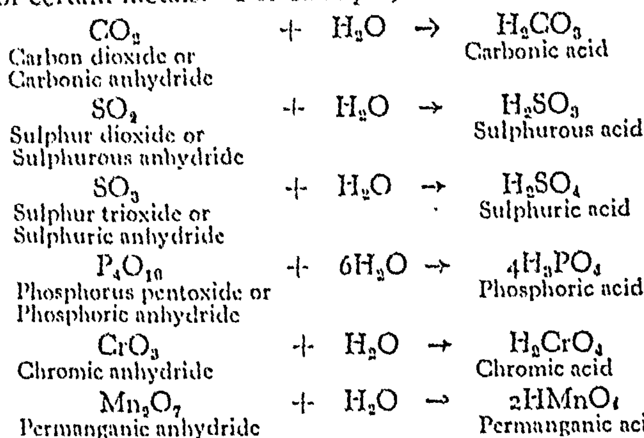
12. **Oxides and their Classification.**—*A binary compound of oxygen with another element is called an* **oxide**. Based on their chemical behaviour or oxygen content, chief classes of oxides are :

BASED ON THEIR CHEMICAL BEHAVIOUR

(a) Based on their chemical behaviour, the oxides have been classified as :

(i) **Acidic Oxides.** Oxides which dissolve in water forming acids and neutralize alkalis are called acidic oxides. They are also

called acid anhydrides and are the oxides of non-metals or higher oxides of certain metals. For example,



$$\underset{\text{Carbon dioxide or Carbonic anhydride}}{CO_2} + H_2O \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

$$\underset{\text{Sulphur dioxide or Sulphurous anhydride}}{SO_2} + H_2O \rightarrow \underset{\text{Sulphurous acid}}{H_2SO_3}$$

$$\underset{\text{Sulphur trioxide or Sulphuric anhydride}}{SO_3} + H_2O \rightarrow \underset{\text{Sulphuric acid}}{H_2SO_4}$$

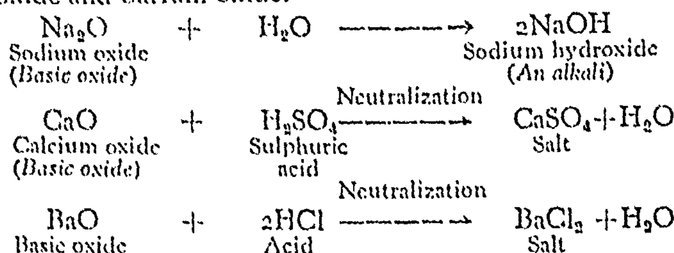
$$\underset{\text{Phosphorus pentoxide or Phosphoric anhydride}}{P_4O_{10}} + 6H_2O \rightarrow \underset{\text{Phosphoric acid}}{4H_3PO_4}$$

$$\underset{\text{Chromic anhydride}}{CrO_3} + H_2O \rightarrow \underset{\text{Chromic acid}}{H_2CrO_4}$$

$$\underset{\text{Permanganic anhydride}}{Mn_2O_7} + H_2O \rightarrow \underset{\text{Permanganic acid}}{2HMnO_4}$$

Here CO_2, SO_2, SO_3, and P_4O_{10} are oxides of non-metals while CrO_3 and Mn_2O_7 are oxides of metals.

(*ii*) **Basic Oxides.** Oxides which dissolve in water forming alkalis or neutralize acids forming salts are called basic oxides or basic anhydrides. These are oxides of metals, *e.g.*, sodium oxide, calcium oxide and barium oxide.

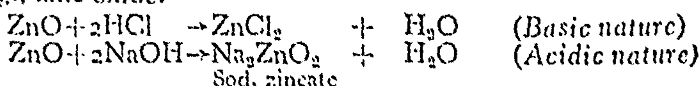


$$\underset{\substack{\text{Sodium oxide}\\(\textit{Basic oxide})}}{Na_2O} + H_2O \longrightarrow \underset{\substack{\text{Sodium hydroxide}\\(\textit{An alkali})}}{2NaOH}$$

$$\underset{\substack{\text{Calcium oxide}\\(\textit{Basic oxide})}}{CaO} + \underset{\text{Sulphuric acid}}{H_2SO_4} \xrightarrow{\text{Neutralization}} \underset{\text{Salt}}{CaSO_4} + H_2O$$

$$\underset{\text{Basic oxide}}{BaO} + \underset{\text{Acid}}{2HCl} \xrightarrow{\text{Neutralization}} \underset{\text{Salt}}{BaCl_2} + H_2O$$

(*iii*) **Amphoteric Oxides.** A few metallic oxides exhibit a dual behaviour. They combine in them the characteristics of both acidic and basic oxides. These form salts both with acids and alkalis, *e.g.*, zinc oxide.



$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \quad (\textit{Basic nature})$$

$$ZnO + 2NaOH \rightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + H_2O \quad (\textit{Acidic nature})$$

Some other amphoteric oxides are aluminium oxide and stannic oxide.

(*iv*) **Neutral Oxides.** Those oxides which are neutral towards litmus are called neutral oxides. Examples of neutral oxides are carbon monoxide (CO), water (H_2O), nitrous oxide (N_2O) and nitric oxide (NO).

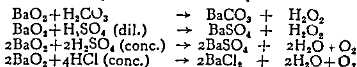
BASED ON THEIR OXYGEN CONTENT

(*b*) Still another basis for classification of oxides is their oxygen content. Based on their oxygen content, the chief classes of oxides are :

(1) **Normal Oxides.** Oxides which contain just as much oxygen as permitted by the valency rule are called normal oxides. A few examples of normal oxides are carbon dioxide (CO_2), sulphur trioxide (SO_3) and litharge (PbO).

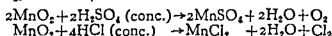
(2) **Poly-oxides.** Oxides containing more oxygen than allowed by valency considerations are termed poly-oxides. These have been further classified as :

(*i*) **True Peroxides.** Those poly-oxides which can be considered to be true salts of hydrogen peroxides are called *True Peroxides*. These produce hydrogen peroxide with dilute acids and liberate oxygen with concentrated acids. A few examples of true peroxides are sodium peroxide and barium peroxide.



$$BaO_2 + H_2CO_3 \rightarrow BaCO_3 + H_2O_2$$
$$BaO_2 + H_2SO_4 \text{ (dil.)} \rightarrow BaSO_4 + H_2O_2$$
$$2BaO_2 + 2H_2SO_4 \text{ (conc.)} \rightarrow 2BaSO_4 + 2H_2O + O_2$$
$$2BaO_2 + 4HCl \text{ (conc.)} \rightarrow 2BaCl_2 + 2H_2O + O_2$$

(*ii*) **Dioxides.** Poly-oxides which contain higher percentage of oxygen like peroxides but do not give any hydrogen peroxide with dilute acids are termed *dioxides*. These oxidise concentrated hydrochloric acid to chlorine and yield oxygen when heated with concentrated sulphuric acid. Manganese dioxide (MnO_2) and lead dioxide (PbO_2) are examples of dioxides.

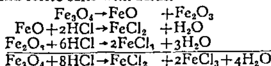


$$2MnO_2 + 2H_2SO_4 \text{ (conc.)} \rightarrow 2MnSO_4 + 2H_2O + O_2$$
$$MnO_2 + 4HCl \text{ (conc.)} \rightarrow MnCl_2 + 2H_2O + Cl_2$$

(3) **Sub-oxides.** Oxides which contain a lower percentage of oxygen than allowed by valency rule are called *sub-oxides, e.g.,* nitrous oxide—N_2O, carbon sub-oxide (C_3O_2).

(4) **Compound oxides** Some oxides may be considered to be made of two simpler oxides. Their chemical behaviour confirms this view. These oxides are called compound oxides. Some examples of this class are *Red lead* (Pb_3O_4) which may be considered to be a mixture of lead dioxide and lead monoxide ($PbO_2 + 2PbO$) and *Ferroso-ferric oxide*, Fe_3O_4 which may be taken as a mixture of ferrous and ferric oxides ($FeO + Fe_2O_3$).

Lead *monoxide (PbO) present in red* lead (Pb_3O_4) *is dissolved* by nitric acid *to form lead nitrate* when lead dioxide, PbO_2 is left undissolved. Similarly Ferroso-ferric oxide, Fe_3O_4 gives a mixture of ferrous and ferric salts with acids.



$$Fe_3O_4 \rightarrow FeO + Fe_2O_3$$
$$FeO + 2HCl \rightarrow FeCl_2 + H_2O$$
$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$
$$\overline{Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O}$$

The two systems for classification of oxides are quite independent of each other. For example, sodium oxide (Na_2O) is a basic oxide as well as a normal oxide. Similarly nitrous oxide (N_2O) is a neutral oxide as well as a sub-oxide.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Ferrous sulphate+Chlorine.
2. Ferrous sulphate+(*i*) Nitrous acid, (*ii*) Nitrogen dioxide.
3. Hydrogen sulphide+(*i*) Chlorine, (*ii*) Acidified potassium dichromate, (*iii*) Ferric chloride.
4. Potassium iodide+Hydrogen peroxide.
5. Lead sulphide+Ozone.
6. Sulphur dioxide+(i) Bromine, (*ii*) Acidified potassium permanganate, (*iii*) Ferric sulphate.
7. Sulphur or Carbon+(i) Nitric acid, (ii) Sulphuric acid.
8. Potassium ferricyanide+Alkaline hydrogen peroxide.
9. Potassium permanganate (*acidified*)+Nitrous acid.
10. Nitric acid+Hydrobromic acid.
11. Sulphuric acid+Hydrobromic acid.
12. Mercuric chloride+Stannous chloride.
13. Zinc oxide+(i) Sulphuric acid, (*ii*) Caustic soda.
14. Barium peroxide+(*i*) Dil. sulphuric acid, (*ii*) Conc. sulphuric acid, (iii) Conc. hydrochloric acid.
15. Manganese dioxide+(i) Conc. sulphuric acid, (*ii*) Conc. hydrochloric acid.
16. Ferroso-ferric oxide+Dilute hydrochloric acid.

QUESTIONS

Essay-type Questions

1. Explain fully oxidation and reduction. Illustrate the oxidising or reducing action of the following :

Hydrogen peroxide ; chlorine ; sulphur dioxide ; hydrogen sulphide.

(Delhi H.S. 1966, 65)

2. Explain the terms 'oxidation' and 'reduction'. Classify the following as oxidising or reducing agents describing in each case two experiments in support :

Bromine ; stannous chloride ; hydrogen sulphide ; sodium nitrite ; potassium permanganate ; potassium dichromate.

(Punjab Pre-Univ. 1962 ; Delhi H.S. 1967)

3. Explain and illustrate the terms 'oxidation' and 'reduction' giving two examples of each. Give examples of two substances which can act best as oxidising and reducing agents. Illustrate their uses with the help of chemical equations. *(Punjab Pre-Univ. 1964 ; U.P. Board Inter. 1960)*

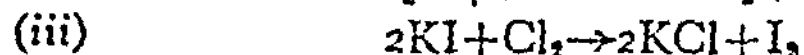
4. In the following reactions explain which reactant is oxidised and which one is reduced. Give reasons for your answer.



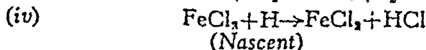
(*i*) $2H_2S+SO_2 \rightarrow 2H_2O+3S$



(*ii*) $MnO_2+4HCl \rightarrow MnCl_2+2H_2O+Cl_2$



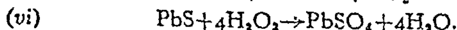
(*iii*) $2KI+Cl_2 \rightarrow 2KCl+I_2$



(*iv*) $FeCl_3+H \rightarrow FeCl_2+HCl$ (*Nascent*)



(*v*) $2CuO+C \rightarrow 2Cu+CO_2$



(*vi*) $PbS+4H_2O_2 \rightarrow PbSO_4+4H_2O$.

5. (*a*) Name any two oxidising agents and two reducing agents. Give reactions which justify their behaviour as oxidising or reducing agents.

(Punjab Pre-Univ. 1971)

(*b*) What tests would you apply to a given substance to show whether it is an oxidising agent or a reducing agent ?

(c) Classify the following substances into oxidising and reducing agents, giving reasons :—

(i) HNO_3, (ii) H_2S, (iii) $SnCl_2$, and (iv) Cl_2.

(d) Give examples of the behaviour of any one substance you know, which can behave both as an oxidising agent and a reducing agent.

6. "Oxidation can never occur without reduction." Explain this giving three examples to illustrate your answer.

7. (a) Explain the term 'Oxidation Number'. What is the oxidation number of :—

(i) S in $Na_2S_2O_3$,

(ii) Mn in $KMnO_4$,

(iii) Cr in $K_2Cr_2O_7$, and

(iv) P in PO_4^{3-} ?

(b) What is the oxidation number of P, Cr and Mn in H_3PO_4, $Na_2Cr_2O_7$ and K_2MnO_4 respectively. (*Punjab Pre-Univ. 1971*)

8. Differentiate between Valency, Oxidation state and Oxidation number.

9. (a) What do you understand by the terms electronation and de-electronation ?

(b) Define oxidation and reduction in terms of :—

(i) loss and gain of electrons, and

(ii) change in oxidation numbers.

10. Mention chief classes of oxides stating the principal characteristics of each class. (*Delhi H.S. 1970*)

11. Write a note on Electrochemical series. (*Bombay Inter. 1962*)

Test Your Understanding

12. In the following statements write T against the true ones and F against those which are false. Rewrite the italicised portions in the false statements to make them true :

(i) Oxidation is a process involving *loss* of electrons.

(ii) During reduction the oxidation number of an element *increases*.

(iii) In CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4, the valency of carbon *changes* but its oxidation number *remains constant*.

(iv) Oxidation is a process involving *increase* in positive valency or *decrease* in negative valency.

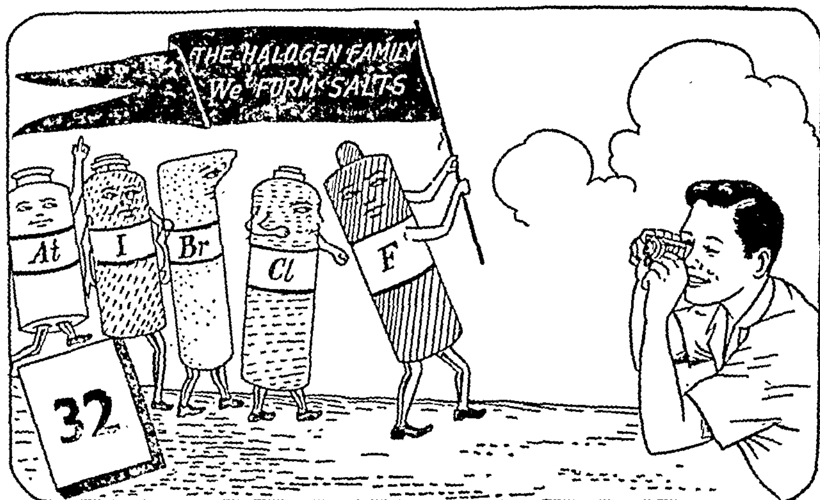
(v) *An oxidising agent* decolorises bromine water or alkaline potassium permanganate

(vi) *A reducing agent* turns starch iodide paper blue.

(vii) Oxidation and reduction *go hand in hand*.

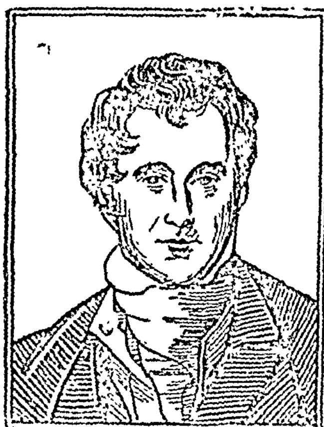
KEY

(i) *T* ; (ii) *F*, decreases ; (iii) *F*, does not change, changes ; (iv) *T*, (v) *F*, a reducing agent ; (vi) *F*, an oxidising agent ; (vii) *T*.



The Halogens

1. General.—The elements fluorine, chlorine, bromine, iodine and astatine constitute one family, called Halogens, a name derived from Greek words meaning "salt producer". They form group VII A of the Periodic Table. They are a closely related family and their inclusion in the same group is justified by their similar electronic configurations, common valency and related physical and chemical properties (*see* page 2·83).



Sir Humphry Davy
(1778—1829)

An English chemist who did much work on fluorine, chlorine and iodine. He proved that fluorine was an element, though he was unable to isolate it.

FLUORINE

2. **Historical.**—**Scheele** prepared hydrofluoric acid in 1771 by heating fluorspar (CaF_2) with sulphuric acid. **Davy** attempted to obtain fluorine by electrolysis of this acid but failed. Anhydrous acid was found to be a non-electrolyte whereas electrolysis of aqueous acid gave only hydrogen and oxygen.

In 1860, **Gore** showed that a solution of anhydrous hydrogen fluoride (KHF_2) in anhydrous hydrofluoric acid conducts electric current. But another difficulty was of the cell and the electrodes. Platinum vessel when used gave a chocolate powder while a carbon vessel changed into a gaseous product.

The isolation of fluorine thus remained for a long time one of the master problems of inorganic chemistry. It was in 1886 that Moissan succeeded in electrolysing a solution of acid potassium fluoride in a platinum-iridium vessel. In 1899 he replaced this vessel by a copper vessel.

3. **Occurrence.**—Fluorine is too active to occur free in nature, in the combined state it occurs as *fluorspar* (CaF_2), *cryolite* (Na_3AlF_6) and *fluorapatite* [$CaF_2.3Ca_3(PO_4)_2$]. Small quantities of fluorine are present as fluoride in the soil, river water, plants and bones and teeth of animals.

4. **Preparation.**—Moissan prepared fluorine by electrolysing a solution of potassium hydrogen fluoride (1 part) in anhydrous [illegible] platinum-iridium [illegible] ter on he found [illegible] becomes coated with a protective coat of copper fluoride which prevents the reaction between copper and fluorine.

It is now more conveniently prepared by electrolysis of fused sodium or potassium hydrogen fluoride (perfectly dry). Electrolysis is carried out between graphite electrodes in a V-shaped electrically heated copper tube (Fig. 32·1). The ends of the tube

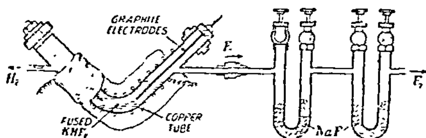
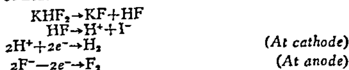


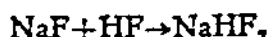
Fig. 32·1—Preparation of fluorine.

are covered with copper caps into which the graphite electrodes are fixed with bakelite cement. The copper tube is thickly lagged to prevent loss of heat.



$$KHF_2 \rightarrow KF + HF$$
$$HF \rightarrow H^+ + F^-$$
$$2H^+ + 2e^- \rightarrow H_2 \quad \textit{(At cathode)}$$
$$2F^- - 2e^- \rightarrow F_2 \quad \textit{(At anode)}$$

Fluorine liberated at the anode is passed through U-tube containing sodium fluoride. This removes the hydrogen fluoride vapours coming with fluorine.



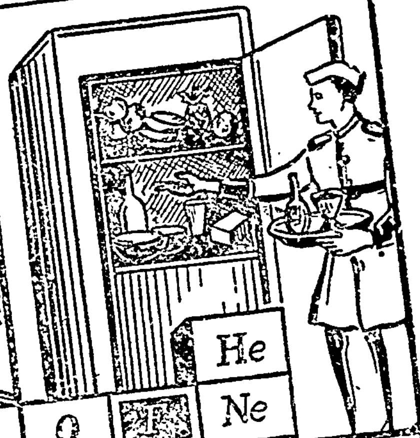
$$NaF + HF \rightarrow NaHF_2$$

THE HALOGEN FAMILY









				He
C	N	O	F	Ne
Si	P	S	Cl	A
Ge	As	Se	Br	Kr
	Sb	Te	I	Xe
	Bi	Po	At	Rn

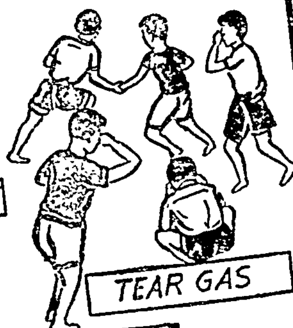
Al, Ga











BROMIDES AND IODIDES

In Whytlaw Gray's method electrolysis of fused potassium hydrogen fluoride is carried out in an electrically heated copper cell which serves as cathode also. A graphite electrode serves as anode and is surrounded by a perforated copper diaphragm. The diaphragm prevents mixing of hydrogen and fluorine which would otherwise react explosively.

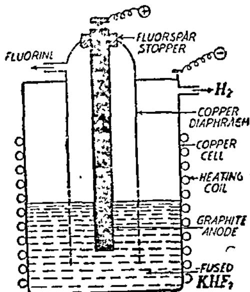


Fig. 32·2—Whytlaw Gray's method for preparation of fluorine.

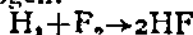
Hydrogen and fluorine are collected as described above.

5. Properties of Fluorine:

(*a*) **Physical.** Fluorine is a pale greenish-yellow, pungent-smelling gas. It is poisonous in nature but not so poisonous as hydrofluoric acid vapour. It is heavier than air. It condenses to a liquid (b.p. −187°C) and crystallizes to a pale yellow solid (m.p. −233°C).

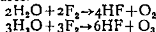
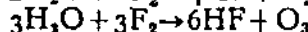
(*b*) **Chemical.** (*i*) **Combination with Elements.** Fluorine is the most active element known and directly combines with most metals and non-metals except oxygen, nitrogen and inert gases. Carbon, phosphorus, sulphur, arsenic, antimony, bromine, iodine and potassium burn spontaneously in the gas with the formation of fluorides. Metals burn in it only on heating. Lead is only slowly attacked at room temperature whereas in case of copper, a protective coating of copper fluoride is obtained.

(*ii*) **Affinity for Hydrogen.** Fluorine combines with moist hydrogen explosively *even in the dark and even at* −252°C. It burns in a jar of hydrogen.



$$H_2+F_2 \rightarrow 2HF$$

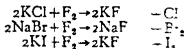
It fumes in moist air and decomposes water forming hydrofluoric acid and liberating oxygen or ozone even in the dark and at very low temperatures.

$$2H_2O+2F_2 \rightarrow 4HF+O_2$$
$$3H_2O+3F_2 \rightarrow 6HF+O_3$$

(*iii*) **Oxidising Action.** It is a strong oxidising agent and attacks organic matter violently.

(*iv*) **Action on Halides.** It liberates chlorine from chlorides, bromine from bromides and iodine from iodides



$$2KCl+F_2 \rightarrow 2KF+Cl_2$$
$$2NaBr+F_2 \rightarrow 2NaF+Br_2$$
$$2KI+F_2 \rightarrow 2KF+I_2$$

(v) Action on Glass. Fluorine attacks glass but slowly.

6. Uses.—Fluorine industry is still in its infancy and th possible uses of the element are being investigated. There are sign that it will be used to prepare derivatives useful as solvents, lubr cants. refrigerants, fire extinguishers, fungicides, germicides, dye and plastics. For example, 'Freon'—a refrigerant, is CCl_2F_2 an Teflon—a plastic, is obtained by polymerisation of C_2F_4. DDF is an efficient fungicide like DDT.

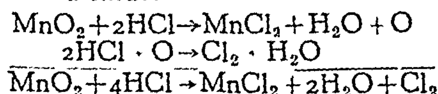
CHLORINE

7. Historical.—Chlorine was discovered in 1774 by Scheele. He pr pared it by heating hydrochloric acid (*muriatic acid*) with manganese dioxi and named it '*oxymuriatic gas*' thinking it to be an oxide of the acid. It w Davy who established its elementary nature in 1810 and called it chlori (Greek, *chloros*=greenish-yellow) because of its colour.

8. Occurrence. In the combined state chlorine is widel distributed as chlorides. Common salt (NaCl) is the most impor tant chloride present in sea water and occurs as rock salt. Stassfur deposits are composed largely of potassium and magnesiun chlorides.

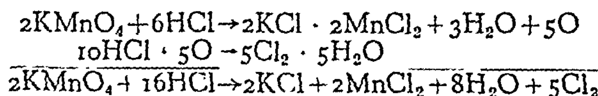
9. Preparation. Chlorine can be prepared by the oxidatio of hydrochloric acid with any of the following oxidising agents.

(i) *Manganese dioxide.*



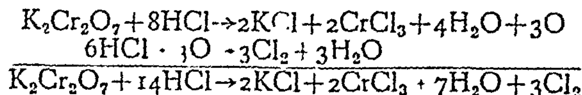
$$MnO_2+2HCl \rightarrow MnCl_2+H_2O+O$$
$$2HCl+O \rightarrow Cl_2+H_2O$$
$$MnO_2+4HCl \rightarrow MnCl_2+2H_2O+Cl_2$$

(ii) *Potassium permanganate.*



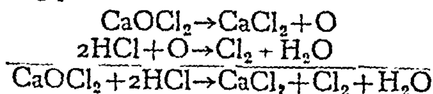
$$2KMnO_4+6HCl \rightarrow 2KCl+2MnCl_2+3H_2O+5O$$
$$10HCl+5O \rightarrow 5Cl_2+5H_2O$$
$$2KMnO_4+16HCl \rightarrow 2KCl+2MnCl_2+8H_2O+5Cl_2$$

(iii) *Potassium dichromate.*



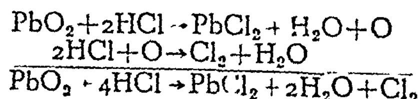
$$K_2Cr_2O_7+8HCl \rightarrow 2KCl+2CrCl_3+4H_2O+3O$$
$$6HCl+3O \rightarrow 3Cl_2+3H_2O$$
$$K_2Cr_2O_7+14HCl \rightarrow 2KCl+2CrCl_3+7H_2O+3Cl_2$$

(iv) *Bleaching powder.*



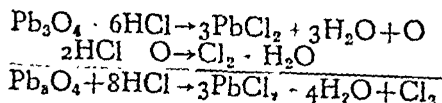
$$CaOCl_2 \rightarrow CaCl_2+O$$
$$2HCl+O \rightarrow Cl_2+H_2O$$
$$CaOCl_2+2HCl \rightarrow CaCl_2+Cl_2+H_2O$$

(v) *Lead dioxide.*



$$PbO_2+2HCl \rightarrow PbCl_2+H_2O+O$$
$$2HCl+O \rightarrow Cl_2+H_2O$$
$$PbO_2+4HCl \rightarrow PbCl_2+2H_2O+Cl_2$$

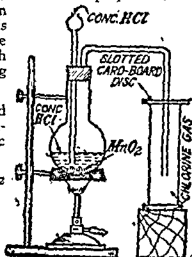
(vi) *Red lead.*



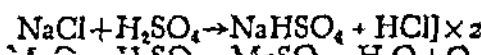
$$Pb_3O_4+6HCl \rightarrow 3PbCl_2+3H_2O+O$$
$$2HCl+O \rightarrow Cl_2+H_2O$$
$$Pb_3O_4+8HCl \rightarrow 3PbCl_2+4H_2O+Cl_2$$

10. Laboratory Preparation of Chlorine.—In the laboratory chlorine is prepared by any of the following methods :

(i) *By heating manganese dioxide with hydrochloric acid.* This is the cheapest laboratory method for the preparation of chlorine. The apparatus used is shown in Fig. 32·3. If needed, the gas is bubbled through water to remove hydrochloric acid gas and then through concentrated sulphuric acid for drying (Fig. 32·4).



A mixture of common salt and concentrated sulphuric acid is commonly used instead of hydrochloric acid.



$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl] \times 2$

2N:

(ii) *By dropping concentrated hydrochloric acid* ... *manganate.* The ... expensive, it is a ... gas. Chlorine ... out any hydrochloric acid gas and further dried by passing through concentrated sulphuric acid.

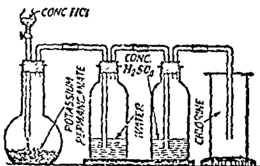
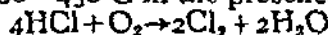


Fig. 32·4—Laboratory preparation of pure dry chlorine.

11. Manufacture of Chlorine.—Chlorine is manufactured by two important processes as given below :

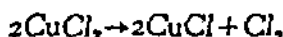
(i) **Deacon's process.** This is an old method for the manufacture of chlorine not used extensively today.

Theory. *The process depends on the fact that hydrochloric acid gas is partially converted into chlorine when heated with oxygen (in air) at 400—450°C in the presence of a catalyst.*

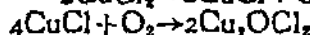


$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

Bricks or porous earthenware impregnated with cupric chloride are used as the catalyst. The action of the catalyst is explained as follows :



$$2CuCl_2 \rightarrow 2CuCl + Cl_2$$



$$4CuCl + O_2 \rightarrow 2Cu_2OCl_2$$



$$Cu_2OCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

Process. One volume of hydrochloric acid gas is mixed with four volumes of air and heated to 450°C. The hot mixture is passed through a tower packed with the catalyst maintained at 450°C (Fig. 32·5). The resulting mixture is cooled, scrubbed with

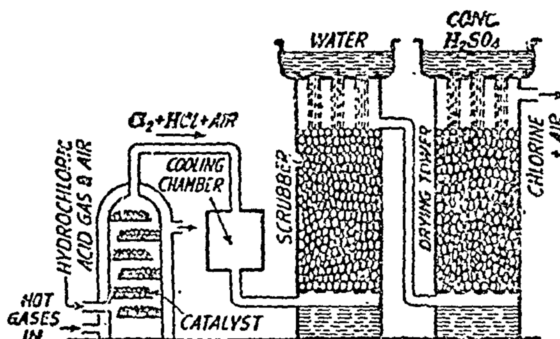
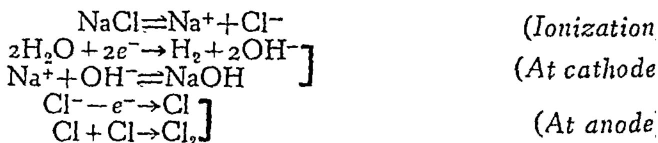


Fig. 32·5—Deacon's process for the manufacture of chlorine.

water to wash out unoxidised hydrogen chloride and dried witl sulphuric acid. Chlorine thus manufactured contains only 5—10% of the gas mixed with nitrogen and a little air. It is too dilute fo liquefaction or storage and is, therefore, mainly used on the spo for the manufacture of bleaching powder.

(*iii*) **Electrolytic process.** At present chlorine is preparec on a commercial scale almost exclusively by the electrolytic pro cess as described below :

Theory. When an electric current is passed through brin (NaCl solution containing Na^+ and Cl^-), Na^+ ions move to th cathode where hydrogen and OH^- ions are formed by reduction o water. Sodium ions combine with OH^- ions to give sodium hydr oxide. The chloride ions, on the other hand, are directed toward the anode where they lose one electron (unit negative charge each and are liberated as chlorine atoms which immediately forn chlorine molecules and are liberated as chlorine gas as follows :



$$NaCl \rightleftharpoons Na^+ + Cl^- \quad \textit{(Ionization}$$

$$\left.\begin{array}{l} 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ Na^+ + OH^- \rightleftharpoons NaOH \end{array}\right] \quad \textit{(At cathode}$$

$$\left.\begin{array}{l} Cl^- - e^- \rightarrow Cl \\ Cl + Cl \rightarrow Cl_2 \end{array}\right] \quad \textit{(At anode}$$

If sodium hydroxide and chlorine so produced are allowed tc come in contact, these will react again and the whole labour will bc wasted.



$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

Hence out of necessity, the construction of the cell should bc such that sodium hydroxide and chlorine once produced do not come in contact with each other.

Process. Based upon the above principle a number of electrolytic cells have been used. The one commonly used is Nelson cell (Fig. 32·6). It consists of a U-shaped perforated steel cathode lined inside with asbestos paper and suspended in a rectangular iron tank. A carbon anode dips in brine placed in the cathode.

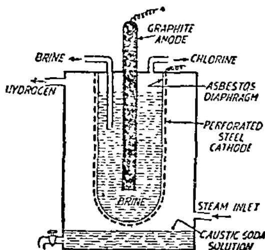


Fig. 32·6—Nelson cell.

On passing electric current chlorine is liberated at the anode and led out through the outlet above and compressed into steel cylinders. Sodium ions penetrate through the asbestos paper and along with OH^- formed by reduction of H_2O at cathode form sodium hydroxide. Sodium hydroxide produced is collected in the outer tank while hydrogen is drawn off through the exit at the top and collected as valuable by-products.

12. Properties of Chlorine.

(a) Physical. (i) It is a greenish-yellow pungent smelling gas heavier than air (about 2½ times as heavy as air).

(ii) It is poisonous in nature. It causes headache if inhaled in small quantities but proves fatal in large quantities.

(iii) It dissolves in water to give chlorine water which smells of chlorine and on cooling deposits greenish-yellow crystals of $Cl_2.8H_2O$.

(iv) It can be easily liquefied by cooling under pressure to a yellow liquid (b.p. $-34·6°C$) which freezes at $-101·6°C$ to a pale-yellow solid. Faraday liquefied chlorine under its own pressure by cooling in a freezing mixture (Fig. 32·7).

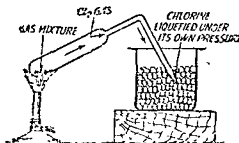
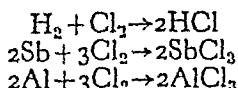


Fig 32·7—Liquefaction of chlorine by cooling under its own pressure.

(b) Chemical. Important chemical properties of chlorine can be discussed under the following headings :

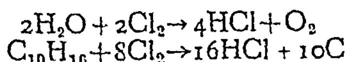
(1) Combination with Elements It is one of the very reactive elements and directly combines with a number of other elements,

e.g., hydrogen (in diffused sunlight) ; phosphorus, antimony powder, sodium and thin copper leaves (when thrown in a jar of chlorine) ; iron aluminium and other metals (when heated in a current of chlorine).



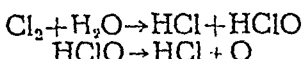
$$H_2 + Cl_2 \rightarrow 2HCl$$
$$2Sb + 3Cl_2 \rightarrow 2SbCl_3$$
$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

(2) **Affinity for Hydrogen.** Chlorine has great affinity for hydrogen. It decomposes water and a burning candle or a filter paper soaked in turpentine oil continues burning in it with deposition of carbon. In each case hydrogen combines with chlorine to give hydrochloric acid.



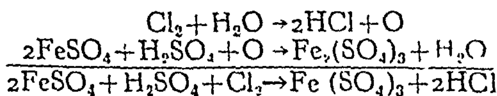
$$2H_2O + 2Cl_2 \rightarrow 4HCl + O_2$$
$$C_{10}H_{16} + 8Cl_2 \rightarrow 16HCl + 10C$$

(3) **Oxidising, Bleaching and Disinfecting action of Chlorine.** It reacts with water to produce hydrochloric acid and hypochlorous acid (HClO). Hypochlorous acid so produced has a tendency to lose nascent oxygen responsible for the oxidizing action of chlorine.

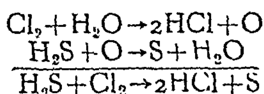


$$Cl_2 + H_2O \rightarrow HCl + HClO$$
$$HClO \rightarrow HCl + O$$

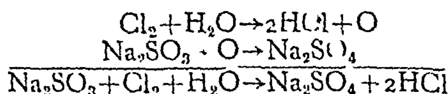
It oxidizes ferrous salts to ferric salts, hydrogen sulphide to sulphur, sulphites and thiosulphates to sulphates, and so on.



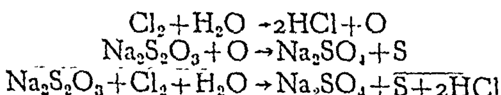
$$Cl_2 + H_2O \rightarrow 2HCl + O$$
$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O$$
$$\overline{2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl}$$



$$Cl_2 + H_2O \rightarrow 2HCl + O$$
$$H_2S + O \rightarrow S + H_2O$$
$$\overline{H_2S + Cl_2 \rightarrow 2HCl + S}$$



$$Cl_2 + H_2O \rightarrow 2HCl + O$$
$$Na_2SO_3 + O \rightarrow Na_2SO_4$$
$$\overline{Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl}$$

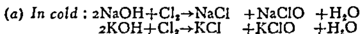


$$Cl_2 + H_2O \rightarrow 2HCl + O$$
$$Na_2S_2O_3 + O \rightarrow Na_2SO_4 + S$$
$$\overline{Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + S + 2HCl}$$

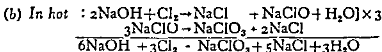
In the presence of moisture, chlorine bleaches vegetable colouring matter like litmus and indigo. During bleaching the vegetable colouring matter combines with nascent oxygen to give a colourless oxidation product. Bleaching effected with chlorine is permanent and the colour is not restored on standing. It is used for bleaching wood pulp and cotton fabrics. Delicate articles like straw, silk, wool, etc., cannot be bleached as they are damaged by chlorine.

It oxidizes organic matter and kills disease germs and is, therefore, extensively used for sterilization of drinking water.

(4) **Action on Alkalis.** In cold chlorine react with alkalis to produce chlorides and hypochlorites while in hot it gives a mixture of chlorides and chlorates.



$$(a)\ \textit{In cold}: 2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$
$$2KOH + Cl_2 \rightarrow KCl + KClO + H_2O$$



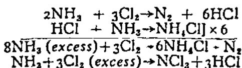
$$(b)\ \textit{In hot}: [2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O] \times 3$$
$$3NaClO \rightarrow NaClO_3 + 2NaCl$$
$$\overline{6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O}$$

With milk of lime (paste of lime in water) it reacts as given above but with slaked lime it gives bleaching powder ($CaOCl_2$).



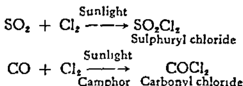
$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \rightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$$

(5) **Action on Ammonia.** With excess of ammonia it gives nitrogen but with excess of chlorine an explosive substance, nitrogen trichloride, is obtained.



$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$
$$[HCl + NH_3 \rightarrow NH_4Cl] \times 6$$
$$\overline{8NH_3\ (\textit{excess}) + 3Cl_2 \rightarrow 6NH_4Cl + N_2}$$
$$NH_3 + 3Cl_2\ (\textit{excess}) \rightarrow NCl_3 + 3HCl$$

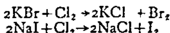
(6) **Formation of Addition Products.** With unsaturated compounds, *e.g.*, sulphur dioxide and carbon monoxide, chlorine forms addition products.



$$SO_2 + Cl_2 \xrightarrow{\text{Sunlight}} \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}$$

$$CO + Cl_2 \xrightarrow[\text{Camphor}]{\text{Sunlight}} \underset{\text{Carbonyl chloride}}{COCl_2}$$

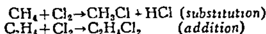
(7) **Action on Halides** Chlorine liberates bromine from bromides and iodine from iodides but has no action on fluorides.



$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$
$$2NaI + Cl_2 \rightarrow 2NaCl + I_2$$

(8) [illegible]

products.



$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl\ \ (\textit{substitution})$$
$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2\ \ (\textit{addition})$$

13. **Uses of Chlorine.**—Chlorine is used :

(1) *For bleaching* wood pulp used for the manufacture of paper and rayon, and for bleaching cotton and linen textiles.

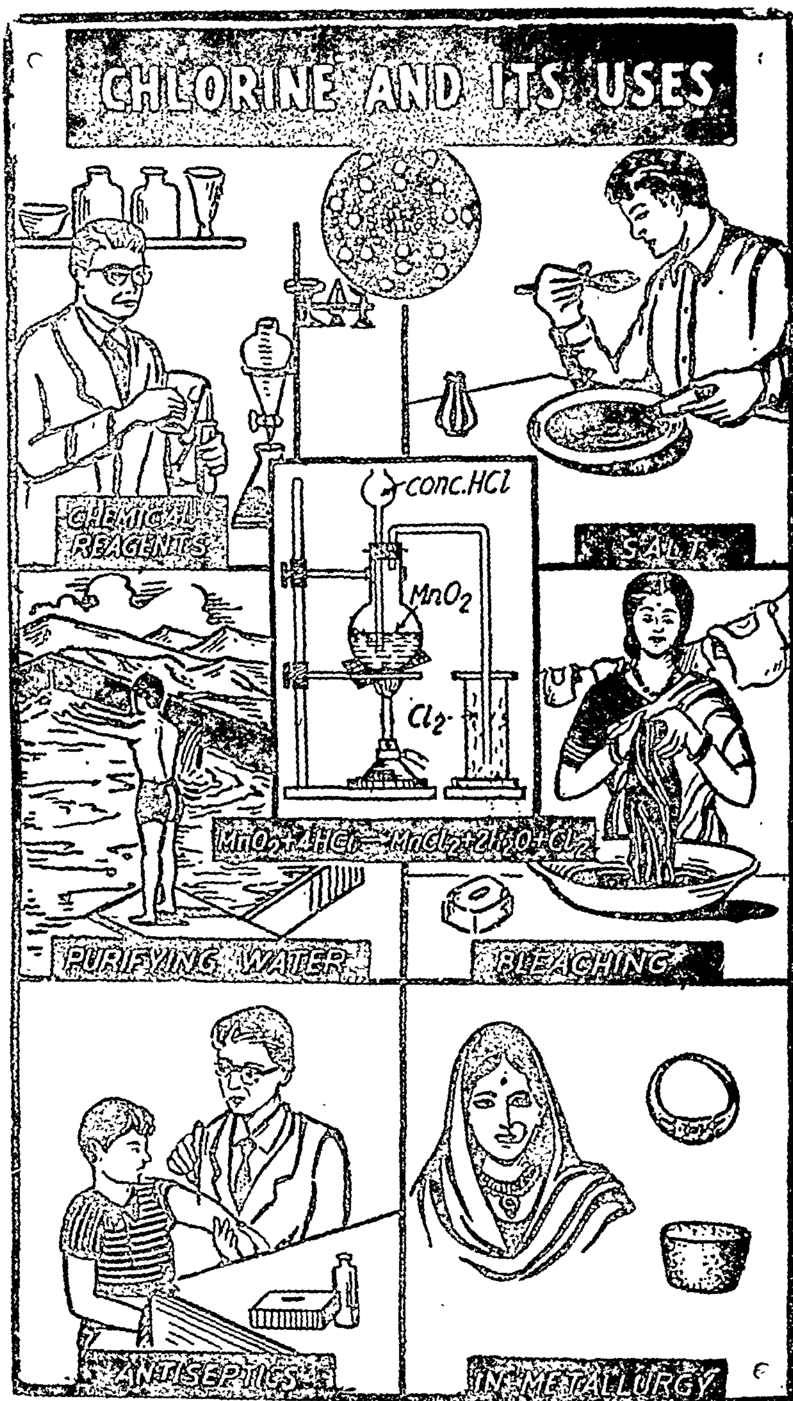

CHLORINE AND ITS USES
CHEMICAL REAGENTS
SALT
conc.HCl
MnO2
Cl2
MnO2+4HCl→MnCl2+2H2O+Cl2
PURIFYING WATER
BLEACHING
ANTISEPTICS
IN METALLURGY

Fig. 32·8

(*ii*) *For purification of drinking water.*

(*iii*) *In organic chemical industry* for the manufacture of chloroform ($CHCl_3$); carbon tetrachloride, (CCl_4) and ethylene chloride ($C_2H_4Cl_2$).

[illegible] for the manufacture of [illegible] perchlorates, bromine

(*v*) *For extraction of metals* like gold and platinum.

(*vi*) *In warfare* for the manufacture of poisonous gases, *e.g.*,

(*a*) Phosgene, $COCl_2$; (*b*) Tear gas, $CCl_3.NO_2$;

(*c*) Mustard gas, $ClC_2H_4-S-C_2H_4Cl$.

14. **Tests for Chlorine.**—Chlorine gas is usually recognized by the following tests :

(*i*) It is a greenish-yellow gas with irritating smell.

(*ii*) It turns starch iodide paper blue.

(*iii*) It bleaches litmus paper and indigo solution.

BROMINE

15. **Historical.**—Bromine was discovered in 1826 by Balard who prepared it by passing chlorine through the mother liquor left after crystallization of common salt from sea water. The element drives its name from the Greek word, *bromos*=a stench.

16. **Occurrence.**—Bromine occurs only in the combined state as bromides of sodium, potassium and magnesium in sea water, certain mineral springs and Stassfurt deposits.

17. **Preparation.**—Bromine is prepared in the laboratory by heating a mixture of concentrated sulphuric acid, manganese dioxide and a bromide in a retort. Bromine distils over and is collected in a cooled receiver (Fig. 32'9).

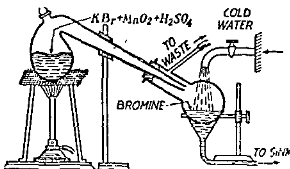
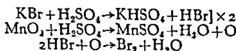
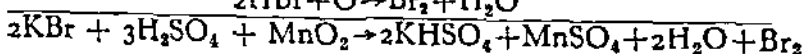


Fig. 32 9—Preparation of bromine in the laboratory .

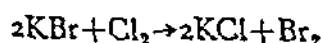


$$KBr+H_2SO_4 \rightarrow KHSO_4+HBr] \times 2$$
$$MnO_2+H_2SO_4 \rightarrow MnSO_4+H_2O+O$$
$$2HBr+O \rightarrow Br_2+H_2O$$



$$2KBr + 3H_2SO_4 + MnO_2 \rightarrow 2KHSO_4+MnSO_4+2H_2O+Br_2$$

It can also be obtained by passing chlorine gas through the solution of a bromide.



$$2KBr+Cl_2 \rightarrow 2KCl+Br_2$$

18. Manufacture.—Mother liquors left after the crystallization of chlorides from carnallite ($KCl.MgCl_2.6H_2O$ from Stassfurt deposits), sea water or certain mineral waters (Ohio Springs in America), contain bromides of sodium, potassium and magnesium.

To manufacture bromine the hot mother liquors are allowed to trickle down a tower packed with earthenware balls while a current of chlorine gas is passed up the tower (Fig. 32·10). Bromine is liberated by the decomposition of bromides by chlorine and passes out through the exit at the top.

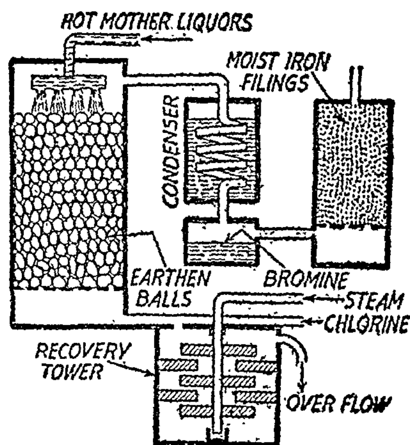
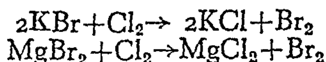


Fig. 32·10—Manufacture of bromine.



$$2KBr+Cl_2 \rightarrow 2KCl+Br_2$$
$$MgBr_2+Cl_2 \rightarrow MgCl_2+Br_2$$

Bromine vapours passing out are passed through a condenser where these condense to a liquid. Any vapours which fail to condense are next passed through a tower packed with moist iron filings where these are absorbed and yield ferroso-ferric bromide.



$$3Fe+4Br_2 \rightarrow Fe_3Br_8$$

The down-coming hot mother liquor carries along with it some bromine in solution and is collected in a tank below fitted with shelf-like partitions. Steam is blown in this tank to recover these bromine vapours. The dissolved bromine and chlorine are blown out by steam. They pass up the tower and are again mixed up with the main current of chlorine.

Bromine so obtained contains chlorine, moisture and small traces of iodine as impurities. It is purified by shaking with cold concentrated sulphuric acid (to remove moisture) and then distilling over potassium bromide (to remove chlorine). Iodine, if present must be removed by treatment with a copper salt when cuprous iodide, CuI is precipitated.

An alternative method for the manufacture of bromine is by electrolysis of the above mother liquors using carbon electrodes Magnesium bromide is decomposed first for even if some magnesium chloride is decomposed, chlorine evolved reacts with magnesium bromide to liberate bromine. Thus it is possible to separate bromine liberated during electrolysis.

19. Properties of Bromine.

(*a*) **Physical.** (*i*) Bromine is a reddish-brown, heavy mobile liquid (Sp. Gr. 3·19).

(*ii*) It boils at 58·5°C and freezes to a yellowish-brown crystalline solid at −7·3°C.

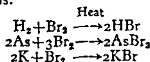
(*iii*) It is fairly soluble in water, more soluble in organic solvents like alcohol, ether, chloroform and carbon disulphide. Bromine water when cooled to 0°C forms bromine hydrate, $Br_2.10H_2O$.

(*iv*) Bromine has an irritating smell and is poisonous in nature. It attacks the skin producing sores which take very long to heal.

(*v*) Bromine colours a starch paper yellow.

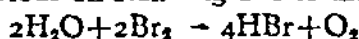
(*b*) **Chemical.** Chemical bromine resembles chlorine in general but is not equally energetic, as shown by its reactions given below:

(1) **Combination with Elements.** Bromine combines direc- [illegible] with it on [illegible] sprinkled [illegible] bines vigorously, sometimes explosively, with phosphorus, potassium and many other metals.



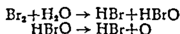
$$H_2+Br_2 \xrightarrow{\text{Heat}} 2HBr$$
$$2As+3Br_2 \longrightarrow 2AsBr_3$$
$$2K+Br_2 \longrightarrow 2KBr$$

(2) **Affinity for Hydrogen.** Bromine has great affinity for hydrogen. It decomposes [illegible] slowly as compared with ch[illegible] mine to give hydrobromic a[illegible] water loses its colour on standing due to this decomposition.



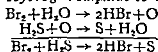
$$2H_2O+2Br_2 \rightarrow 4HBr+O_2$$

[illegible] tion of [illegible] oxygen



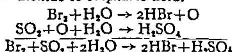
$$Br_2+H_2O \rightarrow HBr+HBrO$$
$$HBrO \rightarrow HBr+O$$

It oxidizes : (*a*) *Hydrogen sulphide to sulphur.*



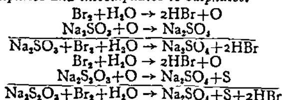
$$Br_2+H_2O \rightarrow 2HBr+O$$
$$H_2S+O \rightarrow S+H_2O$$
$$\overline{Br_2+H_2S \rightarrow 2HBr+S}$$

(*b*) *Sulphur dioxide to sulphuric acid.*



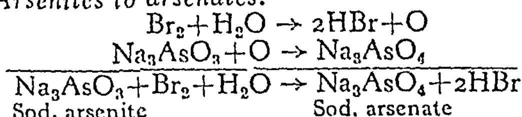
$$Br_2+H_2O \rightarrow 2HBr+O$$
$$SO_2+O+H_2O \rightarrow H_2SO_4$$
$$\overline{Br_2+SO_2+2H_2O \rightarrow 2HBr+H_2SO_4}$$

(*c*) *Sulphites and thiosulphates to sulphates.*



$$Br_2+H_2O \rightarrow 2HBr+O$$
$$Na_2SO_3+O \rightarrow Na_2SO_4$$
$$\overline{Na_2SO_3+Br_2+H_2O \rightarrow Na_2SO_4+2HBr}$$
$$Br_2+H_2O \rightarrow 2HBr+O$$
$$Na_2S_2O_3+O \rightarrow Na_2SO_4+S$$
$$\overline{Na_2S_2O_3+Br_2+H_2O \rightarrow Na_2SO_4+S+2HBr}$$

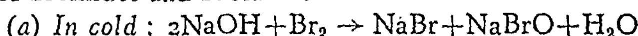
(*d*) *Arsenites to arsenates.*



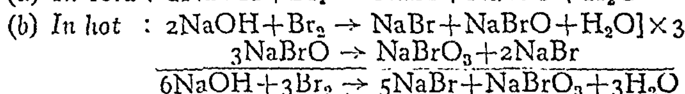
$$Br_2+H_2O \rightarrow 2HBr+O$$
$$Na_3AsO_3+O \rightarrow Na_3AsO_4$$
$$\underset{\text{Sod. arsenite}}{Na_3AsO_3}+Br_2+H_2O \rightarrow \underset{\text{Sod. arsenate}}{Na_3AsO_4}+2HBr$$

Being an oxidizing agent, it also acts as a powerful bleaching agent and a germicide. It bleaches vegetable colouring matter like litmus and indigo.

(4) **Action on Alkalis.** In cold, bromine reacts with alkalis to produce bromides and hypobromites while in hot it gives a mixture of bromides and bromates.



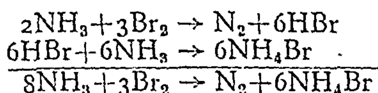
(*a*) *In cold* : $2NaOH+Br_2 \rightarrow NaBr+NaBrO+H_2O$



(*b*) *In hot* : $2NaOH+Br_2 \rightarrow NaBr+NaBrO+H_2O] \times 3$

$$3NaBrO \rightarrow NaBrO_3+2NaBr$$
$$6NaOH+3Br_2 \rightarrow 5NaBr+NaBrO_3+3H_2O$$

(5) **Action on Ammonia.** It oxidizes ammonia to nitrogen.



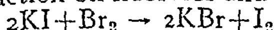
$$2NH_3+3Br_2 \rightarrow N_2+6HBr$$
$$6HBr+6NH_3 \rightarrow 6NH_4Br$$
$$8NH_3+3Br_2 \rightarrow N_2+6NH_4Br$$

(6) **Thermal Dissociation.** Vapour density of bromine corresponds with the formula Br_2 at 228°C. At higher temperatures it dissociates (*e.g.*, at 1050°C, the dissociation is 6·3%).



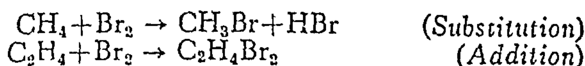
$$Br_2 \rightleftharpoons 2Br$$

(7) **Action on Halides.** Bromine liberates iodine from iodides but has no action on fluorides and chlorides.



$$2KI+Br_2 \rightarrow 2KBr+I_2$$

(8) **Action on Organic Compounds.** With saturated organic compounds, *e.g.*, methane (CH_4), it gives substitution products while with unsaturated ones, e.g., ethylene (C_2H_4), it yields addition products.



$$CH_4+Br_2 \rightarrow CH_3Br+HBr \qquad (\textit{Substitution})$$
$$C_2H_4+Br_2 \rightarrow C_2H_4Br_2 \qquad (\textit{Addition})$$

20. **Uses of Bromine.**—Bromine is used :

(*i*) In the preparation of dyestuffs, disinfectants, bromides, bromites and bromates.

(*ii*) In medicine, sodium and potassium bromides are used as sedatives to quieten the nerves.

(*iii*) In photography, silver bromide which is used in the manufacture of photographic plates, films and papers.

(*iv*) In the manufacture of ethylene bromide is used to increase the efficiency of tetraethyl lead, an anti-knock compound.

(*v*) Bromine compounds like xylyl bromide or bromoacetone are used as tear gases.

(*vi*) As an oxidizing agent in organic synthesis.

21. **Tests for Bromine.** (*i*) Bromine gives pungent-smelling vapours, dark red in colour which do not turn ferrous sulphate solution black (*Distinction from nitrogen dioxide*).

(*ii*) It turns starch paper yellow and starch iodide paper blu...

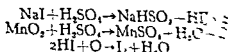
(*iii*) It dissolves in carbon disulphide giving orange colour.

IODINE

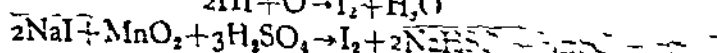
22. **Historical.**—Iodine was discovered by Bernard Courtois (1777–1838), a French chemist. He noticed the purple vapours of iodine during his investigations of ashes from sea weeds. Further investigations were independently carried out by Davy and Gay-Lussac in 1812. The name of the element comes from the Greek word meaning, "violent coloured".

23. **Occurrence.**—Iodine occurs only in the combined state as iodides in California oil well brines, in sea water (traces only), in sea weeds and sponges. Large amounts of iodine are present in *caliche* (crude Chile saltpetre) as sodium iodate. Traces of the element are present in Cod liver oil and human body.

24. Pr... y preparation of iodine is similar ... An iodide is mixed with mangan... sulphuric acid and the vapours are condensed as solid upon the walls of a ... beaker.

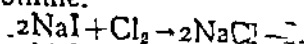


$$NaI+H_2SO_4 \rightarrow NaHSO_4+HI$$
$$MnO_2+H_2SO_4 \rightarrow MnSO_4+H_2O+O$$
$$2HI+O \rightarrow I_2+H_2O$$

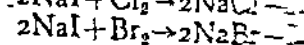


$$2NaI+MnO_2+3H_2SO_4 \rightarrow I_2+2NaHSO_4+MnSO_4+2H_2O$$

(*ii*) It may also be obtained by decomposing ... iodide with chlorine or bromine.



$$2NaI+Cl_2 \rightarrow 2NaCl+I_2$$



$$2NaI+Br_2 \rightarrow 2NaBr+I_2$$

25. **Manufacture of Iodine.**—Principal sources of iodine are: (*i*) Sea weeds, and (*ii*) Caliche or crude Chile saltpetre. It is manufactured from these sources as follows:

(1) From Sea Weeds (*i*) Sea weeds, especially of the *laminaria variety* are collected, dried and burnt in shallow pits to avoid any loss of iodine. The ash called *kelp* contains 0·4—1·3% iodine as iodides in addition to chlorides and sulphates.

(*ii*) The ash is treated with hot water to dissolve out salts. The solution is concentrated when the sulphates separate out followed by chlorides.

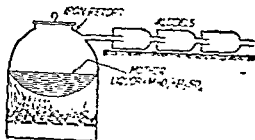
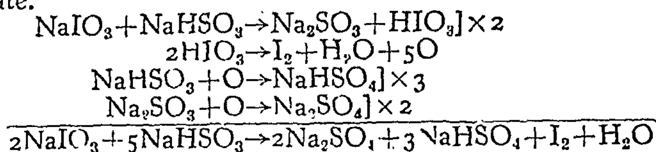


Fig. 32·11—Manufacture of iodine.

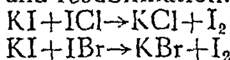
(*iii*) The mother liquor containing iodides is mixed with manganese dioxide and concentrated sulphuric acid and heated in a cast iron retort with lead covers (Fig. 32·11) and connected to stoneware receivers called aludels. On heating, iodine is liberated which sublimes and condenses in the aludels.

(2) **From Caliche.** The mother liquor left after the crystallization of nitre from crude Chile saltpetre contains some iodine as sodium iodate. This is treated with a calculated quantity of sodium bisulphite when iodine is precipitated due to reduction of sodium iodate.



$$NaIO_3+NaHSO_3 \rightarrow Na_2SO_3+HIO_3] \times 2$$
$$2HIO_3 \rightarrow I_2+H_2O+5O$$
$$NaHSO_3+O \rightarrow NaHSO_4] \times 3$$
$$Na_2SO_3+O \rightarrow Na_2SO_4] \times 2$$
$$\overline{2NaIO_3+5NaHSO_3 \rightarrow 2Na_2SO_4+3NaHSO_4+I_2+H_2O}$$

The precipitated iodine is filter-pressed and dried. The commercial iodine contains some iodine chloride (ICl) and iodine bromide (IBr) as impurities. These are removed by distilling iodine over an iodide and resublimation.



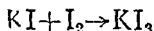
$$KI+ICl \rightarrow KCl+I_2$$
$$KI+IBr \rightarrow KBr+I_2$$

26. **Properties of Iodine.**

(*a*) **Physical.** (*i*) Iodine is a steel-grey solid which sublimes on heating giving beautiful violet-coloured vapours. The rhombic crystalline plates have a metallic lustre.

(*ii*) The vapours have an irritating smell resembling chlorine to some extent.

(*iii*) It is very slightly soluble in water but much more soluble in sodium or potassium iodide solution due to the formation of a tri-iodide.



$$KI+I_2 \rightarrow KI_3$$

The solution behaves as a simple mixture of potassium iodide and free iodine.

Iodine dissolves in carbon disulphide and chloroform giving violet solution (probably due to the presence of free iodine), in other organic solvents, *e.g.*, alcohol, ether, and carbon tetrachloride giving brown solution.

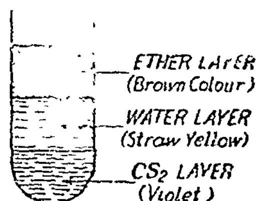
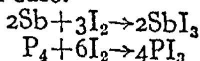


Fig. 32·12.

Expt. 1. In a test tube take some water. Add to this about 1 ml. each of ether and carbon disulphide. Add a few flakes of iodine, shake and allow to stand. Three layers separate as shown in the diagram (Fig. 32·12).

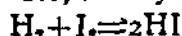
(*b*) **Chemical.** Iodine resembles chlorine and bromine but is less active than either of them as seen from its chemical reactions given on the following pages :

(1) **Combination with Elements.** Iodine directly combines with a number of elements. Antimony powder catches fire when sprinkled in a jar of iodine vapours. Phosphorus and potassium explode in contact with iodine. Mercury and most other metals combine energetically when heated with iodine. Corresponding iodide is obtained in each case.



$$2Sb+3I_2 \rightarrow 2SbI_3$$
$$P_4+6I_2 \rightarrow 4PI_3$$

(2) **Affinity for Hydrogen.** Iodine has much less affinity for hydrogen than other members of its family. It combines with hydrogen only in the presence of a catalyst (heated platinum spiral) and reaction, being reversible, is very slow.

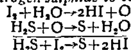


$$H_2+I_2 \rightleftharpoons 2HI$$

It does not decompose water.

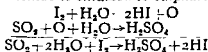
(3) **Oxidizing and Disinfecting Action of Iodine.** Like other halogens, iodine is an oxidizing agent, though much less powerful. For example :

(i) *It oxidizes hydrogen sulphide to sulphur.*



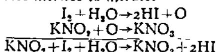
$$\begin{array}{c} I_2+H_2O \rightarrow 2HI+O \\ H_2S+O \rightarrow S+H_2O \\ \hline H_2S+I_2 \rightarrow S+2HI \end{array}$$

(ii) *Sulphur dioxide is oxidized to sulphuric acid.*



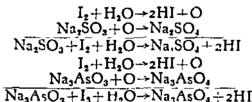
$$\begin{array}{c} I_2+H_2O \rightarrow 2HI+O \\ SO_2+O+H_2O \rightarrow H_2SO_4 \\ \hline SO_2+2H_2O+I_2 \rightarrow H_2SO_4+2HI \end{array}$$

(iii) *It oxidizes nitrites to nitrates*



$$\begin{array}{c} I_2+H_2O \rightarrow 2HI+O \\ KNO_2+O \rightarrow KNO_3 \\ \hline KNO_2+I_2+H_2O \rightarrow KNO_3+2HI \end{array}$$

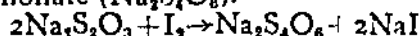
(iv) *It oxidizes sulphites to sulphates and arsenites to arsenates.*



$$\begin{array}{c} I_2+H_2O \rightarrow 2HI+O \\ Na_2SO_3+O \rightarrow Na_2SO_4 \\ \hline Na_2SO_3+I_2+H_2O \rightarrow Na_2SO_4+2HI \end{array}$$

$$\begin{array}{c} I_2+H_2O \rightarrow 2HI+O \\ Na_3AsO_3+O \rightarrow Na_3AsO_4 \\ \hline Na_3AsO_3+I_2+H_2O \rightarrow Na_3AsO_4+2HI \end{array}$$

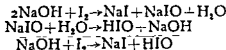
With sodium thiosulphate, iodine reacts quantitatively to give sodium tetrathionate ($Na_2S_4O_6$).



$$2Na_2S_2O_3+I_2 \rightarrow Na_2S_4O_6+2NaI$$

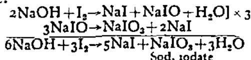
It is not a bleaching agent but is used as a disinfectant and analgesic.

(4) **Action of Alkalis.** In cold dilute solution of an alkali, *iodine reacts to give a hypoiodite which hydrolyses further to yield* hypoiodous acid.



$$\begin{array}{c} 2NaOH+I_2 \rightarrow NaI+NaIO+H_2O \\ NaIO+H_2O \rightarrow HIO+NaOH \\ \hline NaOH+I_2 \rightarrow NaI+HIO \end{array}$$

In hot or even in the cold on standing, iodine reacts with an alkali to give iodate.



$$\begin{array}{c} [2NaOH+I_2 \rightarrow NaI+NaIO+H_2O] \times 3 \\ 3NaIO \rightarrow NaIO_3+2NaI \\ \hline 6NaOH+3I_2 \rightarrow 5NaI+\underset{\text{Sod. iodate}}{NaIO_3}+3H_2O \end{array}$$

(5) **Action on Ammonia.** Iodine reacts with liquor amm to give nitrogen tri-iodide, a black explosive powder.



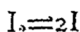
$$2NH_3+3I_2 \rightarrow NI_3.NH_3+3HI$$

Expt. 2. Rub 1 gm. of iodine with liquor ammonia in a glass mo A dark brown precipitate of nitrogen tri-iodide is obtained. Sprinkle it on floor of the lecture hall. It gets soon dried up. As the class goes out, explosions are heard due to decomposition of nitrogen tri-iodide causing fusion among the students.



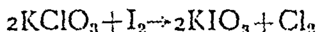
$$8NI_3.NH_3 \rightarrow 5N_2+9I_2+6NH_4I$$

(6) **Thermal Dissociation.** Dissociation of iodine begin 700°C and is complete at 1700°C as shown by vapour density d



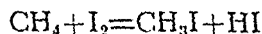
$$I_2 \rightleftharpoons 2I$$

(7) **Action on Halides.** Iodine does not decompose halides but with a concentrated solution of potassium chlorate a little nitric acid it reacts on heating to give potassium iodate.

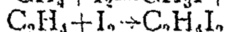


$$2KClO_3+I_2 \rightarrow 2KIO_3+Cl_2$$

(8) **Action on Organic Compounds.** It reacts with or nic compounds but very slowly due to reversible nature of reaction.



$$CH_4+I_2=CH_3I+HI$$



$$C_2H_4+I_2 \rightarrow C_2H_4I_2$$

27. **Uses of Iodine.**—Iodine is largely used—

(i) In the manufacture of iodides (used in medicine photography), iodoform, iodole (antiseptic) and dyestuffs.

(ii) In the form of tincture of iodine and iodex as a disinf tant and analgesic.

Tincture of iodine is prepared by dissolving 15 gm. each of ioc and potassium iodide in 15 gm. of water and making the solution to 500 with rectified spirit (if needed for internal use as in the case of goitre) methylated spirit (if needed for external application).

(iii) In volumetric analysis and as a reagent in the laborator

28. **Tests of Iodine.** (i) Characteristic violet colour of vapour serves as a test for iodine.

(ii) It gives a characteristic blue colour with starch paste paper.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Fluorine+(*i*) Hydrogen, (*ii*) Water, (*iii*) Potassium chlori (*iv*) Sodium bromide, and (*v*) Potassium iodide.

2. Hydrochloric acid+(*i*) Manganese dioxide, (*ii*) Potassium perm ganate, (*iii*) Potassium dichromate, (*iv*) Bleaching powder, (*v*) Lead dioxi and (*vi*) Red lead.

3. Cupric chloride heated.

4. Cuprous chloride+Air.

5. Cuprous oxychloride+Hydrogen chloride.

Property	Fluorine	Chlorine	Bromine	Iodine
1. Atomic weight	19	35.5	80	127
2. At. No and valency	9 ; Monovalent	17 ; Monovalent	35 ; Monovalent	53 ; Monovalent
3. State	Gas	Gas	Liquid	Solid
4. Colour of vapour	Pale yellow	Greenish yellow	Dark reddish brown	Violet
5. Smell	Intensely pungent	Irritating	More so	Intensely so
6. Physical constants	Increase	with the	rise of	Atomic weight
7. Action on hydrogen	Combines even in the dark and cold to give HF	Explosive in light, slow in dark	Combination on heating	Slowly and incomplete on heating, catalyst needed
8. „ „ metals	Forms fluorides	Forms chlorides	Attacks most metals slowly	Reactions slower
9. „ „ non-metals	Combines directly. Exceptions, N_2, O_2, Noble gases	Combines directly. Exceptions, N_2, O_2, Noble gases	Combines with non metals other than N_2, O_2, C, Si.	Only combines with halogens, P, As, and H
10. „ „ water	Decomposes even in the dark and cold to give HF O_2 or O_3	Decomposes slowly to give HCl O_2	Slowly decomposes bright light	No action
11. Oxidizing and bleaching action	Strong oxidising agent destroys organic matter violently	Oxidizes and readily bleaches vegetable colouring matter	Oxidizes and bleaches slowly	Feeble action
12. Action on halides	Displaces Cl_2, Br_2 and I_2 from Cl^- Br^- and I^-	Displaces Br_2 and I_2 from Br^- and I^-	Displaces I_2 from I^- only	No action
13. Action of alkalis		Cold Cl^- and ClO^- Hot Cl^- and ClO_3^-	Cold Br^- and BrO^- Hot Br^- and BrO_3^-	Forms iodides and hypoiodous acid finally iodates in both cases.
14. Stability of Hydracids	Most stable	Stable	Unstable – acts as a reducing agent	Least stable and strong reducing agents
15. Stability of oxyacids	None formed	Least stable	Most stable	Most stable

6. Chlorine+(*i*) Hydrogen, (*ii*) Phosphorus, (*iii*) Iron, (*iv*) Water, (*v*) Turpentine, (*vi*) Ferrous sulphate, (*vii*) Hydrogen sulphide, (*viii*) Sodium sulphite, (*ix*) Sodium thiosulphate, (*x*) Caustic soda, (*xi*) Milk of lime, (*xii*) Slaked lime, (*xiii*) Ammonia, (*xiv*) Sulphur dioxide, (*xv*) Carbon monoxide, (*xvi*) Potassium bromide, (*xvii*) Sodium iodide, (*xviii*) Methane, and (*xix*) Ethylene.

7. Bromine+(*i*) Moist iron filings, (*ii*) Hydrogen, (*iii*) Arsenic, (*iv*) Water, (*v*) Hydrogen sulphide, (*vi*) Sulphur dioxide, (*vii*) Sodium sulphite, (*viii*) Sodium thiosulphate, (*ix*) Sodium arsenite, (*x*) Caustic soda, (*xi*) Ammonia, (*xii*) Potassium iodide, (*xiii*) Methane, (*xiv*) Ethylene.

8. Manganese dioxide and concentrated sulphuric acid mixture heated with (*i*) Sodium chloride, (*ii*) Sodium bromide, (*iii*) Sodium iodide.

9. Potassium iodide+(*i*) Iodine chloride, (*ii*) Iodine bromide.

10. Iodine+(*i*) Antimony, (*ii*) Phosphorus, (*iii*) Hydrogen, (*iv*) Hydrogen sulphide, (*v*) Sulphur dioxide, (*vi*) Potassium nitrite, (*vii*) Sodium sulphite, (*viii*) Sodium thiosulphate, (*ix*) Sodium arsenite, (*x*) Caustic soda, (*xi*) Ammonia, (*xii*) Potassium chlorate, (*xiii*) Methane, (*xiv*) Ethylene.

QUESTIONS

Essay-type Questions

1. The elements Fluorine, Chlorine, Bromine and Iodine form a distinct family of elements referred to as "*The Hologens*". Discuss the statement.

2. Name the members of the halogen family and place them in the order of their rising chemical activity. Support your statement by suitable examples of their chemical reactions.

In what ways are the atomic structures of halogen element alike? If chlorine could take up one more electron in the structure of its atom, how will its properties be affected? (*Delhi H.S. 1964*)

3. "The isolation of fluorine has been one of the major problems in Chemistry." Discuss the statement. Give in outlines the modern method of preparation of fluorine. Draw a neat sketch and mark the various parts of the apparatus used. Mention some important properties of fluorine.

4. (*a*) How is chlorine manufactured? What are its important properties and uses? (*Delhi H.S. 1971, 67; U.P. Board Inter. 1963; All India H.S. 1967; Punjab Pre-University 1971, 64*)

(*b*) How are bleaching powder, sodium hypochlorite and potassium chlorate prepared starting from chlorine? (*Delhi Pre-University 1960; Delhi H.S. 1961, 60*)

(*c*) Compare properties of Chlorine with those of (*i*) Bromine, and (*ii*) Iodine. (*Delhi H.S. 1971, 66; All India H.S. 1969*)

5. Give a convenient method of getting a regular stream of dry chlorine in the laboratory. Explain with the help of equations, the action of chlorine on any five of the following: (*a*) water, (*b*) ammonia, (*c*) carbon monoxide, (*d*) cold and hot solutions of sodium hydroxide, (*e*) a solution of potassium iodide, (*f*) sodium thio-sulphate solution, (*g*) sulphuretted hydrogen, (*h*) methane, (*i*) heated iron, and (*j*) stannous chloride. (*Punjab Pre-Univ. 1971, 61; Delhi H.S. 1971, 60; Nagpur Pre-Univ. 1970*)

6. Describe briefly modern method of manufacture of bromine. Give equations for the reactions of bromine with (*i*) sodium sulphide solution, (*ii*) hot caustic potash solution, and (*iii*) ammonia. How will you distinguish a bromide from an iodide? (*Punjab Pre-Univ. 1970, 62*)

7. What are the principal sources of iodine? How is it prepared from these sources and purified? What happens when iodine is added to a solution of (*a*) hydrogen sulphide, (*b*) sodium thiosulphate, (*c*) potassium iodide? Why does a bottle of hydriodic acid turn brown?

Give an account of its properties, uses and tests. (*Delhi Pre-Medical 1960; Nagpur Pre-Univ. 1971; Punjab Pre-Univ. 1969*)

Test Your Understanding

8 The following statements are made about chlorine Comment on them indicating which of these are correct and which are not Put the incorrect in correct form :

(*a*) It unites with hydrogen to form hydrogen halide of greatest stability.

(*b*) It can be made by electrolysis of its compounds with the non-metallic elements.

(*c*) It is not of much industrial importance except that it is used for chlorinating drinking water. (*Delhi H.S. 1962*)

9. Fill in the blanks in the following :

(i) In the Nelson cell .. and . . .are produced at the cathode by.. ... .

(ii) Chlorine . . . . . . sodium thiosulphate to . ...

(iii) Chlorine combines with SO_2 in presence of . . ...to give.... ... ...

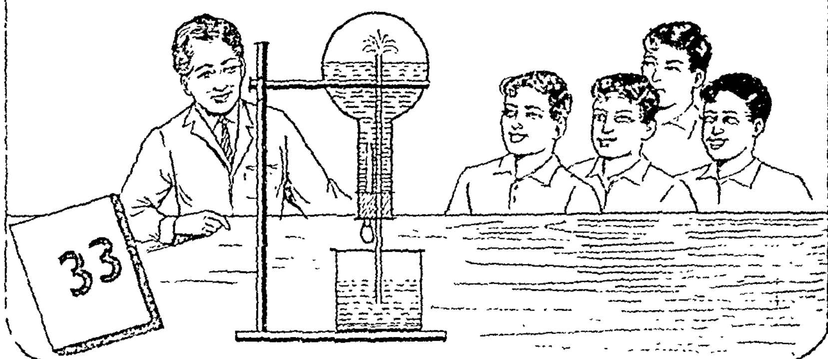
(iv) Bromine reacts with hot KOH to give . . and ... . .

(v) Mother liquor left after crystallization of from crude Chile salt petre contain some iodine as

(vi) Iodine reacts with sodium thiosulphate to give ... . . .

KEY

(i) H_2 ; OH^- ions ; reduction of water. (ii) oxidises, sodium sulphate ; (iii) sun light, SO_2Cl_2 ; (iv) KBr, $KBrO_3$, (v) nitre, $NaIO_3$, (vi) $Na_2S_4O_6$.

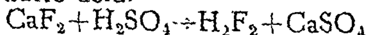


Halogen Acids and Halides

HYDROFLUORIC ACID, H_2F_2

1. **Historical.**—Schwankhard noticed in 1670 that when fluorspar was heated with sulphuric acid, the fumes produced attacked glass. Scheele called it as fluoric acid. It was Ampere in 1810 who suggested that it contained no oxygen and named it hydrofluoric acid analogous to hydrochloric acid.

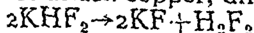
2. **Preparation.**—(*i*) An aqueous solution of hydrofluoric acid is manufactured by heating fluorspar (calcium fluoride) with concentrated sulphuric acid.



$$CaF_2 + H_2SO_4 \rightarrow H_2F_2 + CaSO_4$$

The mixture is heated in a cast-iron retort, the vapours passed through water-cooled condensers and finally absorbed in a series of lead boxes containing water or dilute hydrofluoric acid. It attacks glass ; the commercial acid is, therefore, marketed in gutta-percha, cerasine wax or lead bottles.

(*ii*) Pure acid is prepared in the laboratory by heating pure dry potassium hydrogen fluoride in a platinum retort. Pure acid distils over and is collected in a copper bottle cooled in freezing mixture (pure acid does not attack copper, dilute acid does).



$$2KHF_2 \rightarrow 2KF + H_2F_2$$

3. **Properties of Hydrofluoric Acid.**

(*a*) **Physical.** (*i*) The anhydrous acid is a colourless limpid liquid (b.p. 19·4° and f.p. −102·5°) which fumes strongly in air.

(*ii*) It is highly poisonous, very corrosive to skin and is, therefore, dangerous to manipulate.

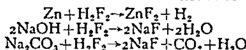
(*iii*) It is very soluble in water with which it gives a constant boiling mixture* containing 36% of the acid and boiling at 120°.

*A 36% solution of hydrofluoric acid boils at 120°C. Composition of the vapours formed is the same as the composition of the liquid mixture. Thus the acid distils unchanged in composition. The dilute acid cannot, therefore, be concentrated by boiling beyond 36%.

(*iv*) Anhydrous acid is a bad conductor of electricity.

(*b*) **Chemical.** (*i*) It is incombustible and non-supporter of combustion.

(*ii*) **Acidic Properties.** It is a weak acid, weaker than phosphoric acid. The anhydrous acid does not attack metals except potassium. A concentrated aqueous solution attacks metals, their oxides, hydroxides or carbonates forming fluorides. Lead is attacked very slightly whereas noble metals are not attacked at all.



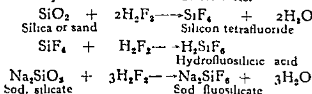
$$Zn + H_2F_2 \rightarrow ZnF_2 + H_2$$
$$2NaOH + H_2F_2 \rightarrow 2NaF + 2H_2O$$
$$Na_2CO_3 + H_2F_2 \rightarrow 2NaF + CO_2 + H_2O$$

(*iii*) **Stability.** Hydrofluoric acid is extremely stable and is not oxidized by strong oxidizing agents or decomposed by heat.

(*iv*) **Action of Silver nitrate and Barium chloride.** With silver nitrate, it gives no precipitate, silver fluoride being soluble in water (*cf.*, other halogen acids). With barium chloride, however, it gives a white precipitate insoluble in dilute nitric acid but soluble in concentrated hydrochloric acid (*cf.*, other halogen acids).

(*v*) **Action of Halogens** Hydrofluoric acid is not decomposed by any of the halogens.

(*vi*) **Action on Glass.** A concentrated aqueous solution of the acid attacks glass (a mixture of silicates) forming silicon tetrafluoride and hydrofluosilicic acid or its salts.



$$\underset{\text{Silica or sand}}{SiO_2} + 2H_2F_2 \longrightarrow \underset{\text{Silicon tetrafluoride}}{SiF_4} + 2H_2O$$
$$SiF_4 + H_2F_2 \longrightarrow \underset{\text{Hydrofluosilicic acid}}{H_2SiF_6}$$
$$\underset{\text{Sod. silicate}}{Na_2SiO_3} + 3H_2F_2 \longrightarrow \underset{\text{Sod. fluosilicate}}{Na_2SiF_6} + 3H_2O$$

(*vii*) It destroys organic matter but does not attack gutta-percha and cerasine wax.

4. **Uses**—(*i*) On account of its action on silica it is used for etching glass. The glass surface is covered with a thin coating of wax and the design to be etched on glass is drawn on the wax surface with a sharp needle. This is exposed to the action of acid or gas and very soon the glass is etched.

(*ii*) It is used for removing silica from artificial graphite and other substances.

(*iii*) In dyeing, double fluorides of antimony and alkali metals have replaced tartar ematic as mordant.

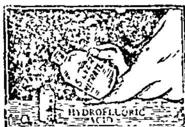


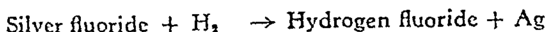
Fig. 33·1—Etching of glass

(*iv*) It is used as an antiseptic in brewing industries, since its effect on yeast is very little as compared with its action on other organisms.

(*v*) The acid is employed for the manufacture of artificial cryolite used in the metallurgy of aluminium.

(*vi*) It is also employed for freeing iron castings from sand.

5. **Composition of Hydrofluoric Acid.**—Gore studied the composition of hydrofluoric acid in 1870. He found that volume of acid obtained by heating silver fluoride with hydrogen was double the volume of hydrogen.



Silver fluoride + H_2 $\rightarrow$ Hydrogen fluoride + Ag

1 vol.	2 vol.
1 mol.	2 mol.
½ mol.	1 mol.
1 atom	1 mol.

In other words 2 vol. of hydrogen fluoride contain 1 vol. of hydrogen.

Applying Avogadro's law, 2 mol. of hydrogen fluoride contain 1 mol. of hydrogen. Or 1 mol. of hydrogen fluoride contains ½ mol. (=1 atom) of hydrogen, *i.e.*, 1 atom of hydrogen is combined with x atoms of fluorine.

Its molecular formula is, therefore, HF_x with mol. wt.$=1+19x$. But its mol. wt. form V.D. (=10) data$=2\times10=20$.

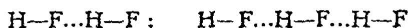
Equating the two values of mol. wt., we get

$$1+19x=20$$

whence $$x=1$$

∴ Molecular formula of hydrogen fluoride is HF.

This was confirmed by its vapour density data at higher temperatures. At lower temperatures its vapour density increases from 10 (at 90°C) to 25·6 (at 26·4°C) to indicate that it occurs as associated molecules H_2F_2 and H_3F_3 at lower temperatures. In the associated molecule the H—F molecules are joined through hydrogen bonds as shown below :



H—F...H—F ; H—F...H—F...H—F

The formula usually adopted is H_2F_2 which is supported by acid salts like KHF_2. In concentrated solutions the acid mainly exists as H_2F_2 whereas in dilute solutions it is present as HF.

6. **Fluorides.**—The salts of hydrofluoric acid are called fluorides. These resemble the other halides (chlorides, bromides and iodides) in many respects. The principal differences between fluorides and other halides are :

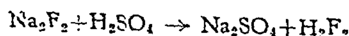
(*i*) Silver fluoride is soluble in water whereas other halides of silver are insoluble.

(*ii*) Calcium and barium fluorides are insoluble in water while chlorides, bromides and iodides of these metals are soluble.

(*iii*) Hydrofluoric acid gives acid fluorides, *e.g.*, KHF_2 and double salts, *e.g.*, Na_3AlF_6 or $3NaF.AlF_3$.

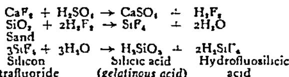
7. **Tetss For Fluorides.**

(1) Heat with concentrated sulphuric acid. Colourless fumes of hydrofluoric acid are evolved which corrode glass and some oily globules appear in the test tube.



$$Na_2F_2+H_2SO_4 \rightarrow Na_2SO_4+H_2F_2$$

(2) Heat with concentrated sulphuric acid and sand. White fumes of silicon titrafluoride are evolved which gelatinise a drop of water held in these fumes. The gelatinous mass is due to the formation of silicic acid.



$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + H_2F_2$$
$$\underset{\text{Sand}}{SiO_2} + 2H_2F_2 \rightarrow SiF_4 + 2H_2O$$
$$\underset{\substack{\text{Silicon}\\ \text{tetrafluoride}}}{3SiF_4} + 3H_2O \rightarrow \underset{\substack{\text{Silicic acid}\\ (\textit{gelatinous acid})}}{H_2SiO_3} + \underset{\substack{\text{Hydrofluosilicic}\\ \text{acid}}}{2H_2SiF_6}$$

(3) Wet tests. (*a*) Fluorides give no precipitate with silver nitrate.

(*b*) With barium chloride, they give white precipitate of barium fluoride insoluble in nitric acid but soluble in concentrated hydrochloric acid (*distinction from sulphates*).

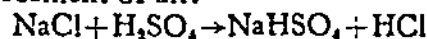
(*c*) *With calcium chloride*, a white precipitate of calcium fluoride is obtained which is soluble in concentrated hydrochloric acid.

HYDROCHLORIC ACID OR HYDROGEN CHLORIDE, HCl

8. Historical.—Hydrochloric acid was known as early as 800 A.D. Glauber prepared it by heating a mixture of common salt and concentrated sulphuric acid in 1648. Priestley called it marine acid while Lavoisier named it as muriatic acid. It was Davy who showed that it was a compound of hydrogen and chlorine and renamed it hydrochloric acid.

9. Laboratory Preparation.—

(i) Hydrochloric acid gas is prepared in the laboratory by heating sodium chloride with concentrated sulphuric acid in a round-bottom flask fitted with a thistle funnel and a delivery tube (Fig. 33·2). The gas being heavier than air is collected by an upward displacement of air.



$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

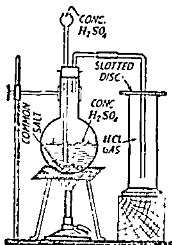
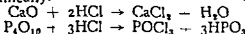


Fig 33·2—Laboratory preparation of hydrochloric acid.

Drying of the gas. Hydrochloric acid gas may be dried, if required, by passing through concentrated, sulphuric acid. Quicklime or phosphorus pentoxide cannot be employed for the purpose as they react with the gas chemically.



$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
$$P_4O_{10} + 3HCl \rightarrow POCl_3 + 3HPO_3$$

Dissolution of the gas in water If the delivery tube is dipped under water, water rushes up due to the high solubility of gas, *i.e.*, back suction occurs and might result in serious explosion While preparing an aqueous solution of the gas, a funnel or pipette is attached to the delivery tube (Fig 33·3) to prevent back suction As some water rises up in the funnel, the outer level falls below the rim the in-coming gas saturates the water sucked up in the funnel and pushes it down

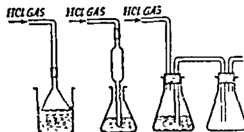


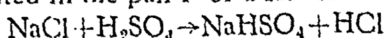
Fig. 33·3—Arrangement to prevent back suction

(ii) It is often conveniently prepared in the laboratory by dropping concentrated sulphuric acid into a commercial sample of concentrated hydrochloric acid in a flask fitted with a delivery tube.

10. **Manufacture.**—Hydrochloric acid is manufactured by the following two methods :

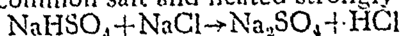
(1) **From Common Salt.** Hydrochloric acid is obtained by the action of hot concentrated sulphuric acid on common salt.

Calculated quantities of common salt and concentrated sulphuric acid are heated in the pan *P* of a salt cake furnace (Fig. 33·4).



$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

Hydrochloric acid gas produced as a result of the above reaction passes out through the exit at the top. Sodium bisulphate (called salt cake) obtained in the reaction is removed from the pan, mixed with more of common salt and heated strongly in the muffle *M*.



$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$

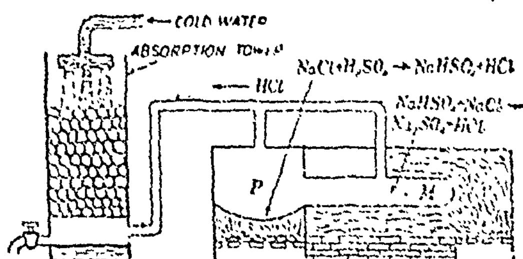
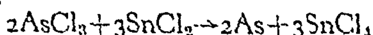


Fig. 33·4—Salt cake furnace for manufacture of Hydrochloric acid.

Hydrochloric acid gas obtained from P and *M* is passed up a tower down which cold water is sprayed when dilute acid is collected at the bottom. This is again sprayed down the tower to absorb more hydrochloric acid gas and get concentrated.

Purification. The acid so manufactured contains a number of impurities, *e.g.*, sulphur dioxide, sulphuric acid, arsenic chloride, ferric chloride and chlorine. It is purified by—

(i) Heating the commercial acid with stannous chloride which removes arsenic.



$$2AsCl_3 + 3SnCl_2 \rightarrow 2As + 3SnCl_4$$

(ii) Treating it with barium chloride which removes sulphuric acid by precipitation followed by distillation, when volatile impurities (sulphur dioxide and chlorine) come out first and are rejected. Pure hydrochloric acid distils over next and is condensed. Ferric chloride is left behind as residue.

(2) **By Synthesis.** Large quantities of hydrogen and chlorine are obtained as by-products during the manufacture of caustic soda by electrolysis of sodium chloride solution. These are dried and made to combine to give hydrogen chloride. Large amounts of the commercial acid today are being obtained by this method.

The plant used is shown in Fig. 33·5. Dry hydrogen is made to burn in an *acid-resisting burner* fitted in a combustion chamber

lined with silica bricks. Dry chlorine is passed into the combustion chamber when hydrogen burns in an atmosphere of chlorine to

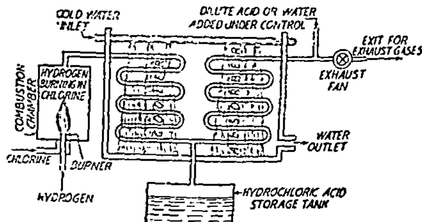


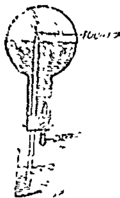
Fig. 33·5—Synthetic [illegible] acid.

give hydrogen chlorid [illegible] cooled by means of spray of [illegible] is next passed up another [illegible] through which water is [illegible] The pipe also is cooled by [illegible] of absorption of hydrogen chloride in water. The solution of hydrochloric acid so obtained flows into the storage tank below. The uncondensed gases are passed through a se[illegible] and the dilute solution [illegible] with water into the first [illegible] right pumps out the waste gases which escape into the atmosphere.

10. Properties of Hydrochloric Acid

(*a*) **Physical.** (i) Hydrochloric acid gas is a colourless, pungent smelling gas with acidic taste

(ii) It fumes in moist air and is extremely soluble in water. One volume of water dissolves 452 volumes of gas at room temperature.



Fountain Expt. Dry a round-bottom flask and fill it with [illegible] a cork [illegible] and a [illegible] litmus [illegible] in the [illegible] rbs hy- [illegible] acuum there. Litmus solution in the beaker is pushed up by atmospheric pressure and it rushes up to give a red fountain inside the flask.

(iii) It is heavier than air.

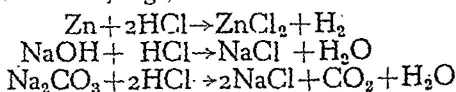
(iv) With water it gives a constant boiling mixture (containing 22·2 per cent of the acid and boiling at 110°C) Dilute solutions of the acid cannot, therefore, be concentrated by boiling beyond 22·2 per cent.

(*v*) It can be easily liquefied to a colourless liquid (b.p. −83°C) and frozen to a white crystalline solid (m.p. —113°C).

(*b*) **Chemical.** (1) It is incombustible and non-supporter of combustion.

(2) **Acidic properties.** (*i*) It is a typical acid but when perfectly dry does not affect litmus. In moist state or in solution, it turns blue litmus red.

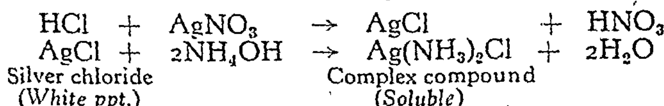
(*ii*) It reacts with metals, their oxides, hydroxides, or carbonates to give chlorides, *e.g.*,



$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

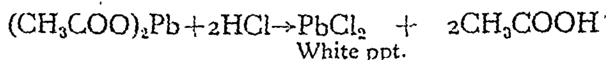
(3) **Stability.** Hydrochloric acid is quite stable and is oxidised only by strong oxidizing agents like manganese dioxide, potassium permanganate, potassium dichromate and lead dioxide or red lead. (*For equations see* page 2·68).

(4) **Action with Silver nitrate and Lead acetate.** With silver nitrate, hydrochloric acid gives a white precipitate insoluble in nitric acid but soluble in ammonium hydroxide.



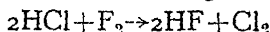
$$HCl + AgNO_3 \rightarrow AgCl + HNO_3$$
$$\underset{\substack{\text{Silver chloride}\\(\textit{White ppt.})}}{AgCl} + 2NH_4OH \rightarrow \underset{\substack{\text{Complex compound}\\(\textit{Soluble})}}{Ag(NH_3)_2Cl} + 2H_2O$$

With lead acetate, it gives a white precipitate soluble in hot water.



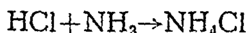
$$(CH_3COO)_2Pb + 2HCl \rightarrow \underset{\text{White ppt.}}{PbCl_2} + 2CH_3COOH$$

(5) **Action of Halogens.** Chlorine is liberated from hydrochloric acid by fluorine but no other halogen can decompose it.



$$2HCl + F_2 \rightarrow 2HF + Cl_2$$

(6) **Action with Ammonia.** Hydrochloric acid gas gives thick white fumes of ammonium chloride with ammonia.



$$HCl + NH_3 \rightarrow NH_4Cl$$

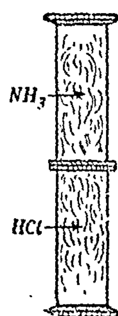


Fig. 33·7.

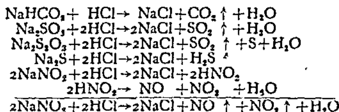
Expt. 2. Dry one gas jar and fill it with dry hydrochloric acid gas. Invert over this another gas jar moistened with a few drops of liquor ammonia (Fig. 33·7). Thick white fumes of ammonium chloride are obtained.

(7) **Aqua regia.** A mixture of three parts of concentrated hydrochloric acid with one part of concentrated nitric acid is called *aqua regia* used for dissolving noble metals, gold and platinum as their chlorides.



$$3HCl + HNO_3 \rightarrow NOCl + 2H_2O + Cl_2$$

(8) **Action on Salts.** Hydrochloric acid decomposes salts of weaker acids, *e.g.*, carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites. *This is used as a dry test for these acid radicals.*



$$NaHCO_3 + HCl \rightarrow NaCl + CO_2\uparrow + H_2O$$
$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + SO_2\uparrow + H_2O$$
$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2\uparrow + S + H_2O$$
$$Na_2S + 2HCl \rightarrow 2NaCl + H_2S\uparrow$$
$$2NaNO_2 + 2HCl \rightarrow 2NaCl + 2HNO_2$$
$$2HNO_2 \rightarrow NO + NO_2 + H_2O$$
$$\overline{2NaNO_2 + 2HCl \rightarrow 2NaCl + NO\uparrow + NO_2\uparrow + H_2O}$$

12. **Uses of Hydrochloric Acid.**—(*i*) It is used for the manufacture of chlorine and chlorides, *e.g.*, ammonium chloride used in dry cells.

(*ii*) In the manufacture of glucose from corn starch.

(*iii*) For extracting glue from bones and purifying bone-black.

(*iv*) A saturated solution of zinc chloride in dilute hydrochloric acid is used for cleaning metals before soldering or plating.

(*v*) As *aqua regia*, it is used for dissolving noble metals.

(*vi*) It is also used in medicine and as a reagent in the laboratory.

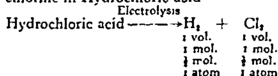
13. **Tests.**—The following characteristic properties of hydrochloric acid

14. **Composition of Hydrochloric Acid**.—(1) Hydrochloric acid is obtained synthetically by exposing a mixture of hydrogen and chlorine to diffused sunlight or burning hydrogen in an atmosphere of chlorine. It gives these two gases on electrolysis. This shows *it is made up of hydrogen and chlorine atoms only*.

(2) Actual composition of hydrochloric acid may be determined in two ways:

(*a*) **Analytical Method.** Electric current is passed through a dilute solution of hydrochloric acid in a Hofmann's voltameter fitted with carbon electrodes. Hydrogen and chlorine are liberated at the two electrodes and have equal volumes.

This shows that one volume of hydrogen combines with one volume of chlorine in Hydrochloric acid



$$\text{Hydrochloric acid} \xrightarrow{\text{Electrolysis}} H_2 + Cl_2$$

	H_2	Cl_2
	1 vol.	1 vol.
	1 mol.	1 mol.
	½ mol.	½ mol.
	1 atom	1 atom

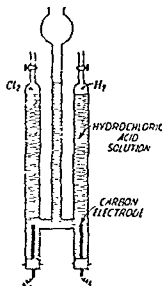


Fig 33·8—Composition of hydrogen chloride (*Analytical method*).

Applying Avogadro's law, we get

One molecule of hydrogen combines with one molecule of chlorine to give the acid.

Or half a molecule (=1 atom) of hydrogen combines with half a molecule (=1 atom) of chlorine, *i.e.*, Empirical formula of the acid is HCl whereas its molecular formula is $(HCl)_x$.

Vapour density of hydrochloric acid gas is 18·25 giving its molecular weight as 36·5 whereas molecular weight as calculated from its molecular formula $(HCl)_x = 36·5x$.

Equating the *two* molecular weights, we have

$$36·5x = 36·5 \quad \text{whence } x = 1.$$

∴ *Molecular formula of Hydrochloric acid is HCl.*

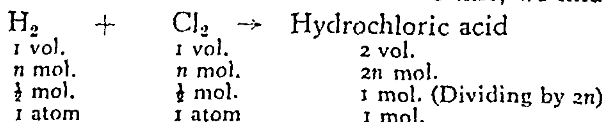
(*b*) **Synthetic Method.** Two tubes of nearly equal capacity are joined through a stop-cock and provided with stop-cocks at the ends (Fig. 33·9). One of them is filled with dry chlorine while the other is filled with dry hydrogen. The two are allowed to mix by opening the middle stop-cock and exposed to diffused sunlight when they combine to give hydrochloric acid gas.

On opening the tube under mercury it is found that neither any gas escapes nor any mercury rises up showing thereby that *when hydrogen and chlorine combine to give hydrochloric acid gas, they do so without change of volume.*

On opening the tube under water it is found that water rushes up and fills the tube completely. This shows that one volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrochloric acid gas. Applying Avogadro's law to this, we find :



Fig. 33·9—Composition of hydrochloric acid (*Synthetic method*)



H_2	+	Cl_2	→	Hydrochloric acid
1 vol.		1 vol.		2 vol.
n mol.		*n* mol.		2*n* mol.
½ mol.		½ mol.		1 mol. (Dividing by 2*n*)
1 atom		1 atom		1 mol.

As explained above, we find that one molecule of hydrochloric acid is made up of one atom of hydrogen and one atom of chlorine, *i.e.*, its formula is HCl.

This is further confirmed by its vapour density data. Its molecular weight as calculated from its V.D. (=18·25) is 36·5 which corresponds to the formula HCl.

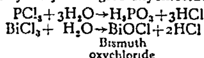
15. **Chlorides.**—The salts of hydrochloric acid are called chlorides. These are also produced by the direct combination of chlorine with elements (*see* page 2·72). Anhydrous chlorides are obtained by passing chlorine or dry hydrochloric acid gas over heated metals. In case a metal gives two chlorides, (*e.g.*, iron,

... g., ferric chloride, stannic
... gives the lower chloride

16. **General Properties of Chlorides**—(i) *State and solubility*. Chlorides are mostly crystalline salts, readily soluble in water. Lead chloride is sparingly soluble whereas mercurous, cuprous and silver chlorides are insoluble in water.

(ii) *Action of heat*. These are stable towards heat but certain hydrated chlorides (*e.g.*, ferric chloride and aluminium chloride) decompose giving out hydrochloric acid. Cupric chloride gives chlorine when heated.

(iii) *Hydrolysis*. Chlorides of non-metals and some metal chlorides react with water. Chlorides of bismuth and antimony undergo partial hydrolysis to give oxychlorides.



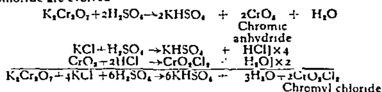
$$PCl_3+3H_2O \rightarrow H_3PO_3+3HCl$$
$$BiCl_3+H_2O \rightarrow \underset{\text{Bismuth oxychloride}}{BiOCl}+2HCl$$

17. **Tests of Chlorides**—(i) When heated with concentrated sulphuric acid, chlorides liberate hydrochloric acid gas which gives thick white fumes with ammonia.

(ii) On heating a small quantity of the chloride mixed with manganese dioxide with concentrated sulphuric acid, chlorine is evolved. It is greenish-yellow in colour and bleaches a moist litmus paper.

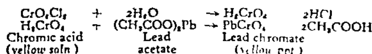
(iii) *Silver nitrate test*. An aqueous solution of a soluble chloride gives a white precipitate with silver nitrate. The precipitate is insoluble in nitric acid but soluble in ammonium hydroxide.

(iv) *Chromyl chloride test*. On heating a mixture of a solid chloride and solid potassium dichromate with concentrated sulphuric acid, red vapours of chromyl chloride are evolved



$$K_2Cr_2O_7+2H_2SO_4 \rightarrow 2KHSO_4+\underset{\text{Chromic anhydride}}{2CrO_3}+H_2O$$
$$[KCl+H_2SO_4 \rightarrow KHSO_4+HCl]\times 4$$
$$[CrO_3+2HCl \rightarrow CrO_2Cl_2+H_2O]\times 2$$
$$K_2Cr_2O_7+4KCl+6H_2SO_4 \rightarrow 6KHSO_4+3H_2O+\underset{\text{Chromyl chloride}}{2CrO_2Cl_2}$$

The red vapours of chromyl chloride, when passed through water, give a yellow solution of chromic acid which gives a yellow precipitate with lead acetate

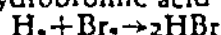


$$CrO_2Cl_2+2H_2O \rightarrow H_2CrO_4+2HCl$$
$$\underset{\substack{\text{Chromic acid}\\ \text{(yellow soln.)}}}{H_2CrO_4}+\underset{\text{Lead acetate}}{(CH_3COO)_2Pb} \rightarrow \underset{\substack{\text{Lead chromate}\\ \text{(yellow ppt.)}}}{PbCrO_4}+2CH_3COOH$$

HYDROBROMIC ACID OR HYDROGEN BROMIDE, HBr

18. **Preparation.**—Different methods which can be employed for the preparation of hydrobromic acid are

(i) **By Synthesis.** A mixture of hydrogen and bromine is passed over an electrically heated platinum spiral when the two combine to give hydrobromic acid (Fig. 33·10).



$$H_2+Br_2 \rightarrow 2HBr$$

(*ii*) **Laboratory Method.** In the laboratory, hydrobromic

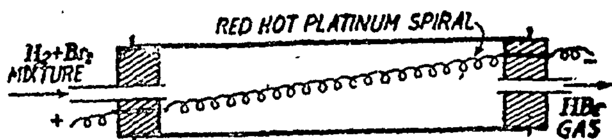


Fig. 33'10.—Synthetic preparation of hydrobromic acid.

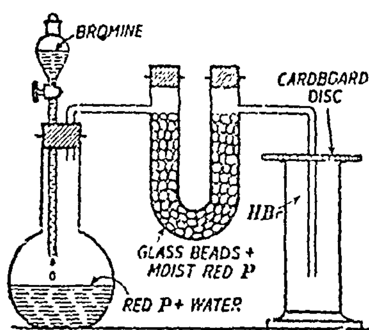
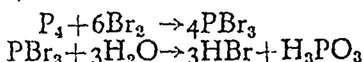


Fig. 33'11—Laboratory preparation of hydrobromic acid.

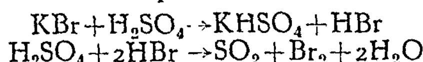
acid is prepared by hydrolysis of phosphorus bromide. Bromine is dropped in a flask containing red phosphorus and water (Fig. 33'11).



$$P_4 + 6Br_2 \rightarrow 4PBr_3$$
$$PBr_3 + 3H_2O \rightarrow 3HBr + H_3PO_3$$

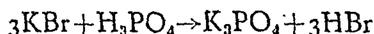
Hydrobromic acid vapours so produced are freed from bromine vapours by passing through a U-tube containing glass beads and *moist red phosphorus.* Hydrogen bromide is finally collected by an upward displacement of air.

Hydrobromic acid cannot be prepared like hydrochloric acid by heating bromide with concentrated sulphuric acid. This is because hydrobromic acid is a strong reducing agent and reduces acid to sulphur dioxide. Thus instead of hydrobromic acid, we get a mixture of bromine and sulphur dioxide.



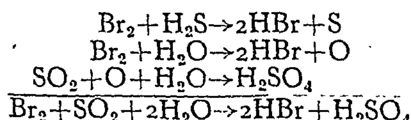
$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$$
$$H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O$$

The acid can, however, be prepared by heating a bromide with concentrated phosphoric acid which is not reduced by hydrobromic acid.



$$3KBr + H_3PO_4 \rightarrow K_3PO_4 + 3HBr$$

(*iii*) **By reduction of Bromine.** A dilute solution of hydrobromic acid can be prepared in the laboratory by bubbling hydrogen sulphide or sulphur dioxide through bromine water till it is decolorised.



$$Br_2 + H_2S \rightarrow 2HBr + S$$
$$Br_2 + H_2O \rightarrow 2HBr + O$$
$$SO_2 + O + H_2O \rightarrow H_2SO_4$$
$$\overline{Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4}$$

19. Properties of Hydrobromic Acid.

(*a*) **Physical.** (*i*) It is a colourless, pungent-smelling gas with acidic taste.

(*ii*) It fumes in moist air and is highly soluble in water.

(*iii*) It is heavier than air and is, therefore, collected by an upward displacement of air.

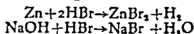
(*iv*) With water it gives a constant boiling mixture containing 48 per cent of the acid and boiling at 126°C.

(*v*) By cooling under high pressure it can be liquefied to a *colourless liquid (b.p. −73°C) which freezes to give a solid (m.p. −87°C).*

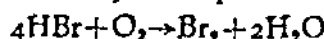
(1) Chemical. It is incombustible and non-supporter of combustion.

(2) Acidic Properties. (*a*) It is a typical acid but does not affect litmus when perfectly dry. In moist state or in solution it turns blue litmus red.

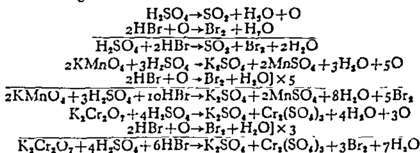
(*b*) It reacts with metals (*e.g.*, iron, zinc or tin), their oxides, hydroxides or carbonates to give bromides.


$$Zn + 2HBr \rightarrow ZnBr_2 + H_2$$
$$NaOH + HBr \rightarrow NaBr + H_2O$$

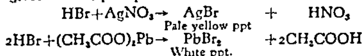
(3) Stability. Hydrobromic acid is not so stable as hydrochloric acid. It is more readily oxidized and thus acts as a strong reducing agent. Dilute solutions of the acid turn yellow due to their oxidation to bromine by atmospheric oxygen.


$$4HBr + O_2 \rightarrow Br_2 + 2H_2O$$

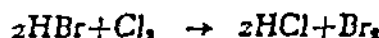
It reduces sulphuric acid to sulphur dioxide, decolorises acidified potassium permanganate solution and turns potassium dichromate solution green.


$$H_2SO_4 \rightarrow SO_2 + H_2O + O$$
$$\underline{2HBr + O \rightarrow Br_2 + H_2O}$$
$$H_2SO_4 + 2HBr \rightarrow SO_2 + Br_2 + 2H_2O$$
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$\underline{2HBr + O \rightarrow Br_2 + H_2O] \times 5}$$
$$2KMnO_4 + 3H_2SO_4 + 10HBr \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Br_2$$
$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
$$\underline{2HBr + O \rightarrow Br_2 + H_2O] \times 3}$$
$$K_2Cr_2O_7 + 4H_2SO_4 + 6HBr \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Br_2 + 7H_2O$$

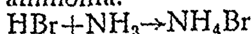
(4) *Action with Silver nitrate and Lead acetate.* With silver nitrate it gives a pale yellow precipitate insoluble in nitric acid and sparingly soluble in ammonium hydroxide. With lead acetate it gives a white precipitate soluble in hot water.


$$HBr + AgNO_3 \rightarrow \underset{\text{Pale yellow ppt}}{AgBr} + HNO_3$$
$$2HBr + (CH_3COO)_2Pb \rightarrow \underset{\text{White ppt.}}{PbBr_2} + 2CH_3COOH$$

(5) Action of Halogens. Bromine is liberated from hydrobromic acid by fluorine and chlorine but iodine has no action.


$$2HBr + Cl_2 \rightarrow 2HCl + Br_2$$

(6) **Action with Ammonia.** It gives white fumes of ammonium bromide with ammonia.



$$HBr + NH_3 \rightarrow NH_4Br$$

20. **Uses.**—Hydrobromic acid does not find any industrial use. It is used as a laboratory reagent in organic chemistry.

21. **Bromides.**—Salts of hydrobromic acid are called bromides *and are very similar to chlorides, principal difference* between the two being that bromides are more readily oxidized than chlorides.

22. Tests for Bromides.—(i) On heating with concentrated sulphuric acid, a bromide liberates a mixture of hydrobromic acid and bromine (red vapour which do not turn ferrous sulphate black).

(ii) With manganese dioxide and concentrated sulphuric acid, bromine vapours are evolved.

(iii) An aqueous solution of a bromide gives with silver nitrate a straw yellow precipitate of silver bromide. This is insoluble in nitric acid and sparingly soluble in ammonium hydroxide.

(*iv*) Bromine is liberated from a bromide solution with chlorine water or a few drops of acidified potassium permanganate. A few drops of carbon disulphide are added to the same solution when an orange colour is obtained in the lower carbon disulphide layer.

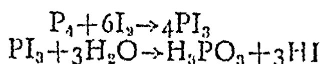
HYDRIODIC ACID OR HYDROGEN IODIDE, HI

23. **Synthesis.**—Hydriodic acid is obtained when hydrogen and iodine mixture is heated in a tube containing finely divided platinum as catalyst.



$$H_2 + I_2 \rightleftharpoons 2HI$$

24. **Laboratory Preparation.**—(i) It is prepared in the laboratory by the action of water on a mixture of red phosphorus and iodine.



$$P_4 + 6I_2 \rightarrow 4PI_3$$
$$PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$$

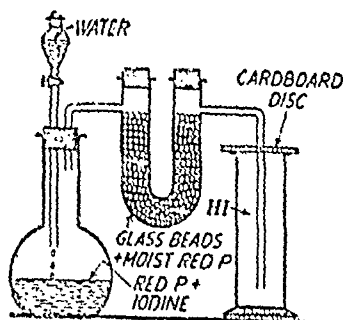
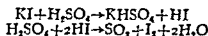


Fig. 33·12—Laboratory preparation of hydrio dic acid.

Water is dropped from a dropping funnel on a mixture of red phosphorus (1 part) and iodine (5 parts) placed in a flask (Fig. 33·12). Hydriodic acid evolved is passed through a U-tube containing glass bead s and moist red phosphorus and finally collected by an upward displacement o air.

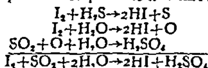
Hydriodic acid cannot be prepared like hydrochloric acid by heating an iodide with concentrted sulphuric acid. This is because hydriodic acid is a strong reducing agent and reduce sulphuric acid to sulphur dioxide. Thus insteed of hydrochloric acids get a mixture of sulphur dioxide and iodine vapours.

To the Student. Properties of hydriodic acid are similar to the properties of hydrobromic acid. Compare the properties of hydrochloric, hydrobromic and hydriodic acids.



$$KI + H_2SO_4 \rightarrow KHSO_4 + HI$$
$$H_2SO_4 + 2HI \rightarrow SO_2 + I_2 + 2H_2O$$

(*ii*) A dilute solution of the acid can be prepared by bubbling hydrogen sulphide or sulphur dioxide through iodine solution.



$$I_2 + H_2S \rightarrow 2HI + S$$
$$I_2 + H_2O \rightarrow 2HI + O$$
$$SO_2 + O + H_2O \rightarrow H_2SO_4$$
$$\overline{I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4}$$

25. Properties of Hydriodic Acid :

(*a*) Physical. (*i*) It is a colourless, pungent smelling gas with acidic taste.

(*ii*) It fumes in moist air and is highly soluble in water.

(*iii*) It is heavier than air.

(*iv*) With water it gives a constant boiling mixture (b p. 127°C) containing 57 per cent of the acid.

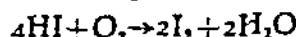
(*v*) It can be easily liquefied and solidified (b.p. −35°C ; m.p. −50·9°C).

(*b*) Chemical. (1) It is incombustible and a non-supporter of combustion.

(2) Acidic properties. (*a*) An aqueous solution of the acid or moist gas turns blue litmus red.

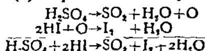
(*b*) With metals, their oxides, hydroxides or carbonates, it gives iodides.

(3) Stability. Of the halogen acids, hydriodic acid is the least stable. It is readily oxidized and thus acts as a strong reducing agent. The aqueous solution turns yellow on standing due to its decomposition in air and light.



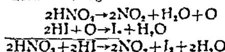
$$4HI + O_2 \rightarrow 2I_2 + 2H_2O$$

It reduces—(*a*) *Sulphuric acid to sulphur dioxide.*



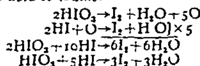
$$H_2SO_4 \rightarrow SO_2 + H_2O + O$$
$$2HI + O \rightarrow I_2 + H_2O$$
$$\overline{H_2SO_4 + 2HI \rightarrow SO_2 + I_2 + 2H_2O}$$

(*b*) *Nitric acid to nitrogen dioxide.*



$$2HNO_3 \rightarrow 2NO_2 + H_2O + O$$
$$2HI + O \rightarrow I_2 + H_2O$$
$$\overline{2HNO_3 + 2HI \rightarrow 2NO_2 + I_2 + 2H_2O}$$

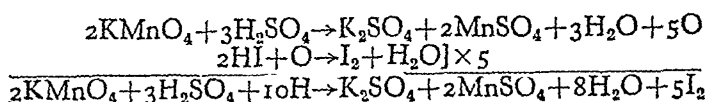
(*c*) *Iodic acid to iodine.*



$$2HIO_3 \rightarrow I_2 + H_2O + 5O$$
$$[2HI + O \rightarrow I_2 + H_2O] \times 5$$
$$\overline{2HIO_3 + 10HI \rightarrow 6I_2 + 6H_2O}$$

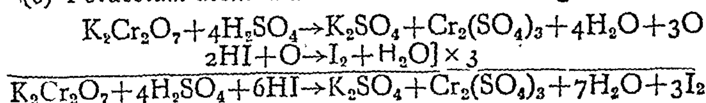
or $$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$

(*d*) *It decolorises acidified potassium permanganate solution.*



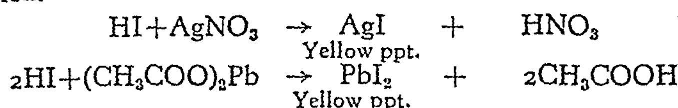
$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5O$$
$$[2HI+O \rightarrow I_2+H_2O] \times 5$$
$$2KMnO_4+3H_2SO_4+10H \rightarrow K_2SO_4+2MnSO_4+8H_2O+5I_2$$

(*e*) *Potassium dichromate solution is turned green.*



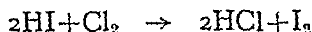
$$K_2Cr_2O_7+4H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O$$
$$[2HI+O \rightarrow I_2+H_2O] \times 3$$
$$K_2Cr_2O_7+4H_2SO_4+6HI \rightarrow K_2SO_4+Cr_2(SO_4)_3+7H_2O+3I_2$$

(4) **Action with Silver nitrate and Lead acetate.** It gives a yellow precipitate with silver nitrate, insoluble both in nitric acid and ammonium hydroxide. With lead acetate it gives a yellow precipitate of lead iodide soluble in hot water giving a colourless solution.



$$HI+AgNO_3 \rightarrow \underset{\text{Yellow ppt.}}{AgI} + HNO_3$$
$$2HI+(CH_3COO)_2Pb \rightarrow \underset{\text{Yellow ppt.}}{PbI_2} + 2CH_3COOH$$

(5) **Action of Halogens.** Iodine is liberated from hydriodic acid by fluorine, chlorine and bromine.



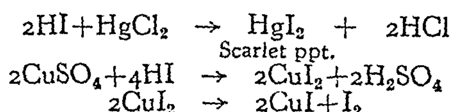
$$2HI+Cl_2 \rightarrow 2HCl+I_2$$

(6) **Action with Ammonia.** It gives white fumes with ammonia.



$$HI+NH_3 \rightarrow NH_4I$$

(7) **Some properties of Hydriodic acid not shown by Hydrochloric or Hydrobromic acid.** It produces a scarlet ppt of mercuric iodide with mercuric chloride and liberates iodine with copper sulphate solution due to the decomposition of cupric iodide first formed to cuprous iodide and iodine.



$$2HI+HgCl_2 \rightarrow \underset{\text{Scarlet ppt.}}{HgI_2} + 2HCl$$
$$2CuSO_4+4HI \rightarrow 2CuI_2+2H_2SO_4$$
$$2CuI_2 \rightarrow 2CuI+I_2$$

26. **Uses.**—Hydriodic acid is used as a reducing agent in organic chemistry.

27. **Iodides.**—Salts of hydriodic acid are called iodides and resemble chlorides. They can be prepared by similar methods.

The iodides are less volatile than the corresponding chlorides and bromides. On heating most of them decompose with the liberation of iodine. Many of them possess characteristic colours. Iodides are used in medicine, photography and as laboratory reagents.

28. Tests.—(i) When heated with concentrated sulphuric acid, they give out hydriodic acid and iodine (violet vapours turning starch paper blue).

(ii) On heating with manganese dioxide and sulphuric acid iodine vapours are evolved.

Distinguishing Tests between the four Halides

Tests	Fluorides	Chlorides	Bromides	Iodides
1. Heat with concentrated sulphuric acid.	HF vapours evolved which corrode glass; oily globules seen in solution.	HCl gas evolved; gives white fumes with NH_3.	$HBr + Br_2$ evolved, starch paper turned yellow; $FeSO_4$ not affected by brown vapours.	$HI + I_2$ evolved. Violet vapours turn starch paper blue.
2. Heat with MnO_2 + conc. sulphuric acid.	Do	Cl_2 gas evolved; greenish yellow, bleaches indigo solution.	Br_2 evolved; tested as above.	I_2 evolved; tested as above.
3. Salt solution + silver nitrate.	No ppt.	White ppt. insol. in HNO_3 but sol. in NH_4OH.	Straw yellow ppt. insol. in HNO_3 sparingly soluble in NH_4OH.	Yellow ppt. soluble both in HNO_3 and NH_4OH.
4. Salt solution + lead acetate solution.	No ppt.	White ppt. soluble in hot water.	White ppt. soluble in hot water.	Yellow ppt. soluble in hot water giving colourless solution.
5. Salt solution + $CaCl_2$.	White ppt. of CaF_2 soluble in conc. HCl.	No ppt.	No ppt.	No ppt.
6. Confirmatory Tests.	Heat with sand and conc. H_2SO_4. White fumes evolved which gelatinise a drop of water exposed to them.	Heat with conc. H_2SO_4 and solid $K_2Cr_2O_7$. Reddish brown vapours of CrO_2Cl_2 evolved. These dissolve in water giving yellow solution which gives a yellow ppt. with lead acetate.	Add chlorine water and carbon disulphide. An orange colour in the lower CS_2 layer.	(i) Add chlorine water and carbon disulphide. A violet colour in the lower CS_2 layer. (ii) A scarlet ppt. with HgI_2, soluble in excess of iodide.

(*iii*) With chlorine water or acidified potassium permanganate, iodine is liberated which gives a violet colour with carbon disulphide.

(*iv*) With silver nitrate, they give a yellow precipitate of silver iodide insoluble in both nitric acid and ammonium hydroxide.

(*v*) With lead acetate, a yellow precipitate soluble in hot water is obtained.

(*vi*) With mercuric chloride, they yield a scarlet precipitate of mercuric iodide soluble in excess of potassium iodide solution.

(*vii*) Iodine is liberated when copper sulphate solution is added to an iodide solution.

29. Distinguishing tests between the Four Halides.—*These are given on page 2·101.*

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Sand+Hydrofluoric acid.

2. Silicon tetrafluoride+water.

3. Sulphuric acid heated with (i) Sodium fluoride, (*ii*) Sodium chloride, (*iii*) Sodium bromide, (*iv*) Sodium iodide.

4. Hydrochloric acid+(i) Zinc, (*ii*) Caustic soda, (*iii*) Silver nitrate, (*iv*) Lead acetate, (*v*) Fluorine, (*vi*) Ammonia, (*vii*) Nitric acid, (*viii*) Sodium thiosulphate, (*ix*) Sodium sulphide, (*x*) Sodium nitrate, (*xi*) Sodium sulphite.

5. Water+(i) Phosphorus trichloride, (*ii*) Bismuth chloride, (*iii*) Phosphorus and bromine, (*iv*) Phosphorus and iodine.

6. Chromyl chloride test for a chloride.

7. Bromine or Iodine+(i) Hydrogen sulphide, (ii) Sulphur dioxide.

8. Hydrobromic acid+(i) Zinc, (*ii*) Sodium carbonate, (*iii*) Air, (*iv*) Potassium permanganate, (*v*) Potassium dichromate, (*vi*) Silver nitrate, (*vii*) Lead acetate, (*viii*) Chlorine, (*ix*) Ammonia.

9. Hydriodic acid+(i) Air, (ii) Sulphuric acid, (*iii*) Nitric acid, (*iv*) Iodic acid, (*v*) Potassium permanganate, (*vi*) Potassium dichromate, (*vii*) Silver nitrate, (*viii*) Lead acetate, (*ix*) Chlorine, (*x*) Ammonia, (*xi*) Mercuric chloride, (*xii*) Copper sulphate.

QUESTIONS

Essay-type Questions

1. (*a*) How is hydrofluoric acid prepared ? What action has this acid on silica and to what use is this property of the acid put in industry ?

(*b*) How is anhydrous hydrofluoric acid prepared ? Compare its properties with hydracids of other halogen elements. (*Delhi Pre-Medical 1964*)

(*c*) Write a short note on Etching. (*Punjab H.S. 1961*)

2. (*a*) Describe with the help of a neat diagram the manufacture of hydrochloric acid. How is the acid purified ? Give reactions of the acid on (*i*) Potassium dicromate, (*ii*) Silver nitrate, and (*iii*) Concentrated nitric acid.

(*b*) What is the action of concentrated hydrochloric acid on (i) MnO_2, (*ii*) $KMnO_4$ and (*iii*) $Na_2S_2O_3$? (*Punjab Pre-Univ. 1970*)

3. How is hydrochloric acid gas prepared in the laboratory ? Give a neat sketch of the apparatus used. Give an experiment to show its extreme solubility. What is the action of acid on (*a*) Silver nitrate, (*b*) Calcium carbonate, (*c*) Ammonia ? (*Punjab H.S. 1962*)

4. How is pure hydrogen chloride prepared ? Describe experiments to determine the composition of hydrochloric acid gas both by analysis and synthesis of the substance. Why is the determination by the method of analysis alone not regarded as a sufficient and rigorous proof of its composition.

5. How is pure hydrobromic acid prepared? How does it differ from hydrofluoric acid and how can it be distinguished from (a) HCl, (b) HI?

6. (a) Describe giving a neat diagram the preparation of hydriodic acid in the laboratory. Illustrate the reducing properties of the acid. Compare the properties of this acid with those of hydrochloric acid.

(b) Give equations for the reaction of hydriodic acid with:

(i) Sulphuric acid, (ii) Mercuric chloride, (iii) Copper sulphate.

(*Punjab Pre-Univ.* 1971)

7. Compare and contrast the preparation and properties of hydrochloric, hydrobromic and hydriodic acids. (*U.P. Board Inter.* 1960)

8. Describe with the help of equations the distinguishing tests of (i) chlorides and iodides, (ii) fluoride from a chloride.

Test Your Understanding

9. Read carefully the arguments given below and see if you can reproduce the same in your own words:

(a) Thermal stability of halogen acids decreases from HF to HI.

(i) This is because bond strength decreases gradually from H—F to H—I.

(ii) Bond strength is related to bond length which increases from H—F to H—I. Bond strength decreases as bond length increases.

(b) Acid strength of halogen acids increases gradually from HF to HI.

(i) Weak acid strength of HF is due to very strong H—F bond.

(ii) Acid strength increases as the H—X bond strength decreases.

10. Fill in the blanks:

(a) Glass is etched by..... as .....are acted upon by it.

(b) High solubility of HCl can be demonstrated by .. experiment.

(c) AgCl dissolves in NH_4OH due to the formation of.. .

(d) Potassium iodide and mercuric chloride solutions react to produce......

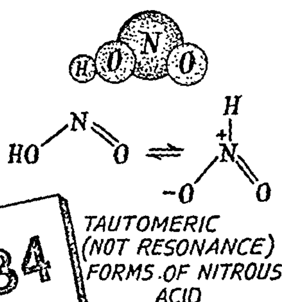
(e) When HI is added to copper sulphate solution a. .. precipitate is formed due to the formation of.. ...

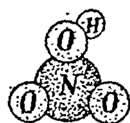
(f) Strongest acid amongst halogen acids is .....

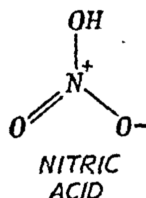
KEY

10. (a) HF, silicates and SiO_2 (b) fountain (c) complex $[Ag(NH_3)_2]^+$ (d) K_2HgI_4 (first a red precipitate of HgI_2) (e) brownish, a mixture of $CuI+I_2$. (f) HI.

OXY-ACIDS OF NITROGEN







Oxy-Compounds of Chlorine

1. **Oxides and Oxy-acids of Chlorine.**—Chlorine gives three well known oxides and four oxy-acids. These are :

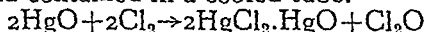
Oxides	Oxy-Acids
Chlorine monoxide, Cl_2O	Hypochlorous acid, $HClO$
Chlorine dioxide, ClO_2	Chlorous acid, $HClO_2$
Chlorine heptoxide, Cl_2O_7	Chloric acid, $HClO_3$
	Perchloric acid, $HClO_4$

In the oxy-acid the acid strength increases gradually from $HClO$ to $HClO_4$. It will be interesting to note that the acid strength increases with the increase in the oxidation number of chlorine which increases from $+1$ in $HClO$ to $+3$ in $HClO_2$, $+5$ in $HClO_3$ and $+7$ in $HClO_4$.

The more important ones out of these are described below :

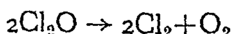
2. **Chlorine monoxide, Cl_2O.**

Preparation. Chlorine monoxide is obtained by passing dry chlorine over freshly precipitated yellow oxide of mercury previously ignited and contained in a cooled tube.



$$2HgO+2Cl_2 \rightarrow 2HgCl_2.HgO+Cl_2O$$

Properties. It is a brownish yellow gas which condenses to an orange-coloured liquid (b.p. 2°C). It decomposes readily on heating or in contact with organic matter. Liquid chlorine monoxide may explode if the test tube containing it is scratched with a file.



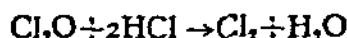
$$2Cl_2O \rightarrow 2Cl_2+O_2$$

It dissolves in water giving golden yellow solution of hypochlorous acid. It is, therefore, the anhydride of hypochlorous acid.



$$Cl_2O+H_2O \rightleftharpoons 2HClO$$

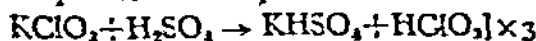
It is a strong oxidizing agent. Hydrochloric acid decomposes it as given below :



$$Cl_2O + 2HCl \rightarrow Cl_2 + H_2O$$

3. **Chlorine dioxide, ClO_2.**

Preparation. Chlorine dioxide is prepared by the action of concentrated sulphuric acid on potassium chlorate.



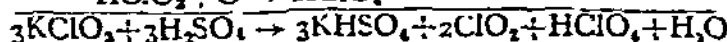
$$[KClO_3 + H_2SO_4 \rightarrow KHSO_4 + HClO_3] \times 3$$



$$2HClO_3 \rightarrow 2ClO_2 + H_2O + O$$



$$HClO_3 + O \rightarrow HClO_4$$



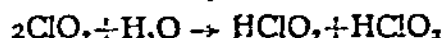
$$3KClO_3 + 3H_2SO_4 \rightarrow 3KHSO_4 + 2ClO_2 + HClO_4 + H_2O$$

[illegible] potassium chlorate to about 1 ml. [illegible] Warm it very cautiously, [illegible] yellow gas with pungent [illegible] hot needle in the gas, it explodes.

Properties. (*i*) It is a deep yellow pungent-smelling gas. The gas can be condensed to a dark-red liquid (b.p. 11°C).

(*ii*) The gas or the liquid explodes violently when heated. It is a powerful oxidizing and bleaching agent.

(*iii*) With water it gives a mixture of chlorous and chloric acids. It is thus a mixed anhydride of these acids.

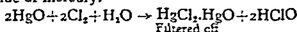


$$2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$$

4. **Hypochlorous Acid, HClO.**

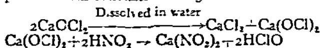
Preparation. The acid is known only in solution which can be prepared in any of the following ways :

(*i*) By shaking chlorine water with freshly precipitated yellow oxide of mercury.



$$2HgO + 2Cl_2 + H_2O \rightarrow \underset{\text{Filtered off}}{HgCl_2.HgO} + 2HClO$$

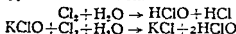
(*ii*) It may be more conveniently prepared by adding slowly a calculated quantity of 5 per cent nitric acid to a clear solution of bleaching powder with constant stirring.



$$2CaOCl_2 \xrightarrow{\text{Dissolved in water}} CaCl_2 + Ca(OCl)_2$$

$$Ca(OCl)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2HClO$$

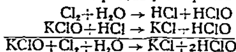
(*iii*) Hypochlorous acid is formed by the action of chlorine on water or a hypochlorite solution.



$$Cl_2 + H_2O \rightarrow HClO + HCl$$

$$KClO + Cl_2 + H_2O \rightarrow KCl + 2HClO$$

The last reaction is probably completed in two steps.

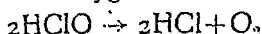


$$Cl_2 + H_2O \rightarrow HCl + HClO$$

$$KClO + HCl \rightarrow KCl + HClO$$

$$KClO + Cl_2 + H_2O \rightarrow KCl + 2HClO$$

Properties. It is highly unstable and readily decomposes into hydrochloric acid and oxygen.



$$2HClO \rightarrow 2HCl + O_2$$

Due to the ease with which it liberates nascent oxygen ($HClO \rightarrow HCl + O$), it acts as a powerful oxidizing and bleaching agent. On distillation it decomposes to give water and its anhydride, Cl_2O.



$$2HClO \rightarrow Cl_2O + H_2O$$

It neutralizes alkalis to form salts called hypochlorites. Two important hypochlorites are sodium hypochlorite and bleaching powder.

5. Sodium hypochlorite, NaClO.

Preparation. (i) Sodium hypochlorite is prepared by passing chlorine through a dilute solution of caustic soda in cold.



$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

(*ii*) Various textile mills use sodium hypochlorite solution called *bleaching solution* for bleaching purposes. They prepare it by electrolysis of brine in an undivided cell. Sodium liberated at the cathode reacts with water to give caustic soda which reacts with chlorine liberated at the anode to give sodium hypochlorite.

The type of cell commonly employed for the preparation of bleaching solution is shown in Fig. 34·1. It consists of two earthenware troughs, *X* and *Y*, one placed inside the other. The inner trough *X* is fitted with 25—30 vertical graphite electrodes. The end electrodes are connected with the positive and negative terminals of a 110 volt main. Each one of the outer electrodes acts as a cathode on one face and anode on the other due to induction. Both the troughs are filled with brine. Cold water is circulated through a cooling pipe dipped in the outer tank. This serves to keep the temperature of the electrolyte below 24°C

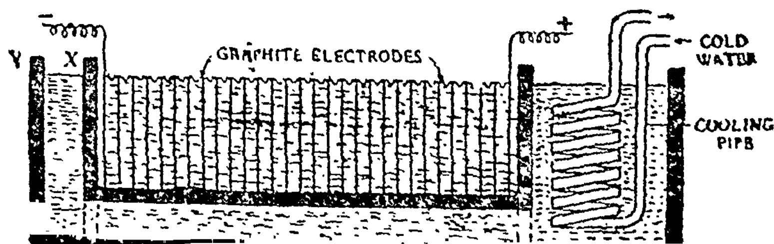
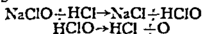


Fig. 34·1—Electrolytic cell for the preparation of bleaching solution.

On passing electric current bleaching solution is obtained according to the equation given above. As the hydrogen liberated at the cathodes bubbles through the solution (in *X*), it overflows into the outer trough *Y*. At the same time some fresh solution from *Y* is sucked into *X* through an opening in the base. The circulation of the electrolyte continues till the end.

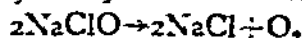
Properties. (*i*) *With dilute acids.* Sodium hypochlorite liberates hypochlorous acid and thus acts as a powerful oxidizing and bleaching agent.



$$NaClO + HCl \rightarrow NaCl + HClO$$
$$HClO \rightarrow HCl + O$$

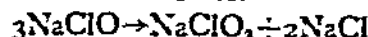
(Nascent oxygen is responsible for oxidising and bleaching action)

(*ii*) *Decomposition.* On standing it loses oxygen and this decomposition is catalysed by cobalt chloride.



$$2NaClO \rightarrow 2NaCl + O_2$$

(*iii*) *Auto-oxidation.* At higher temperature it undergoes auto-oxidation to form sodium chlorate.



$$3NaClO \rightarrow NaClO_3 + 2NaCl$$

6. Bleaching powder or Chloride of Lime, $CaOCl_2$.

Preparation. Bleaching powder is manufactured by the ... not a single ... hypochlorous



$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \rightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$$

Slaked lime is added in the hopper at the top and moved forward by the revolving blades from one cylinder to the next till it falls down. At the same time dilute chlorine obtained generally by the Deacon's Process is passed up.

Slaked lime and chlorine, moving in opposite direction as they are, ensure complete conversion. This is called Principle of counter currents. More and more chlorine passing up is absorbed by down-coming lime till in the uppermost cylinder the last traces of chlorine are absorbed by fresh lime. Thus out-going gases do not contain any chlorine. Similarly exhausted lime in the lowermost cylinder reacts with fresh chlorine and is completely converted into bleaching powder. It is collected in the receiver below.

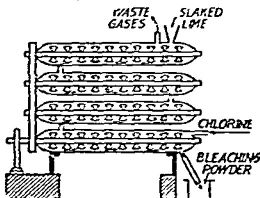
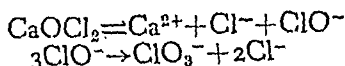


Fig 34·2—Hasenclever plant for the manufacture of bleaching powder.

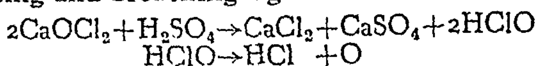
Properties. (1) It is a yellowish white powder which gives a strong smell of chlorine. It is soluble in cold water. Small insoluble portion always left is lime present in it.

(*ii*) When shaken with cold water and filtered, the cold filtrate gives the reactions of chlorides and hypochlorite ions while on heating it shows the presence of chloride and chlorate ions.



$$CaOCl_2 \rightleftharpoons Ca^{2+} + Cl^- + ClO^-$$
$$3ClO^- \rightarrow ClO_3^- + 2Cl^-$$

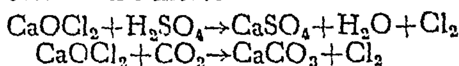
(*iii*) **With insufficient dilute acids.** Bleaching powder on treatment with small quantities of a dilute acid liberates hypochlorous acid which can easily furnish nascent oxygen and thus acts as an **oxidising and bleaching agent.**



$$2CaOCl_2 + H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HClO$$
$$HClO \rightarrow HCl + O$$

It oxidises lead salts to lead dioxide and converts alcohol into chloroform.

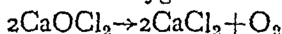
(*iv*) **With excess of dilute acid.** On treating bleaching powder with excess of dilute acid or even carbon dioxide the whole of chlorine present in the molecule is evolved.



$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$
$$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$$

The amount of chlorine thus set free is called "available chlorine." Bleaching powder is priced according to the amount of available chlorine in the sample. A good sample contains 35·38% of available chlorine.

(*v*) **Decomposition.** In the presence of a little cobalt chloride it decomposes to liberate oxygen.



$$2CaOCl_2 \rightarrow 2CaCl_2 + O_2$$

On long standing, it undergoes slow auto-oxidation.



$$6CaOCl_2 \rightarrow Ca(ClO_3)_2 + 5CaCl_2$$

Uses. Bleaching powder is used : (*i*) Chiefly for bleaching cotton, linen and wood pulp in textile and paper factories. Delicate articles like straw, silk or ivory are injured by chlorine and are, therefore, bleached with milder bleaching agents like hydrogen peroxide and not with bleaching powder.

(*ii*) As a disinfectant and germicide and for sterilization of drinking water.

(*iii*) In rendering wool unshrinkable.

(*iv*) For the manufacture of chloroform.

(*v*) As an oxidising agent in many chemical industries.

7. **Process of Bleaching.**—In big factories bleaching is an automatic process. The article to be bleached, say, a roll of cotton cloth, is first boiled with a dilute caustic soda solution. This removes any grease or wax from the fibres. The strip of cloth is then drawn with the help of pulley arrangement, through several vats as given below :

(*i*) The first vat contains a solution of bleaching powder or bleaching solution obtained by electrolysis of cold dilute brine in

an undivided cell. Some bleaching occurs here probably through the action of atmospheric carbon dioxide which liberates hypochlorous acid, a bleaching agent.

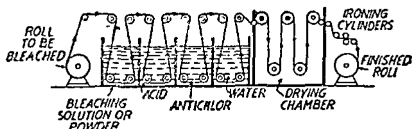


Fig. 34·3—Bleaching of cotton cloth in big factories with bleaching powder or bleaching solution.

(ii) The second vat contains a dilute acid solution. The acid liberates chlorine from the bleaching solution and thus completes the bleaching started in the first vat.

(iii) The third vat contains the solution of an antichlor, *e.g.*, sodium bisulphite or hypo used to destroy the last traces of chlorine sticking to the fibre. Chlorine injures the fibre, if not destroyed quickly after bleaching is over.



$$NaHSO_3 + Cl_2 + H_2O \rightarrow NaHSO_4 + 2HCl$$

(*iv*) This strip of cloth is next washed thoroughly in the fourth vat containing water It is dried as it passes through the drying cylinders and ironed in the ironing cylinders.

Thus a roll of unbleached cloth is being unwrapped on the *left and the bleached cloth after drying and ironing is being* wrapped on a roll on the right.

8. **Constitution of Bleaching Powder.**

(i) Dalton (1813) suggested bleaching powder to be a loose combination of quicklime (CaO) and chlorine but chlorine is not absorbed by quicklime, hence the view was rejected.

(ii) Chlorine and sodium hydroxide react as follows :



$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

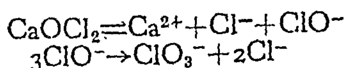
On the analogy of this reaction Balard suggested in 1835 that *bleaching powder is an equimolecular mixture of calcium chloride* and calcium hypochlorite. In that case it should possess properties of both calcium chloride and calcium hypochlorite which is not the case as shown below ·

(*a*) Calcium chloride is hygroscopic but bleaching powder is not so.

(*b*) Calcium chloride is soluble in alcohol but no portion of bleaching powder is soluble in alcohol.

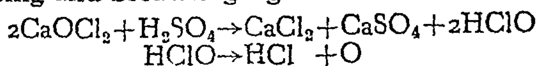
weak acids while
leaching powder

(*ii*) When shaken with cold water and filtered, the cold filtrate gives the reactions of chlorides and hypochlorite ions while on heating it shows the presence of chloride and chlorate ions.



$$CaOCl_2 \rightleftharpoons Ca^{2+} + Cl^- + ClO^-$$
$$3ClO^- \rightarrow ClO_3^- + 2Cl^-$$

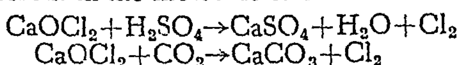
(*iii*) **With insufficient dilute acids.** Bleaching powder or treatment with small quantities of a dilute acid liberates hypochlorous acid which can easily furnish nascent oxygen and thus acts as an **oxidising and bleaching agent.**



$$2CaOCl_2 + H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HClO$$
$$HClO \rightarrow HCl + O$$

It oxidises lead salts to lead dioxide and converts alcohol int chloroform.

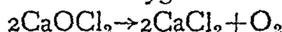
(*iv*) **With excess of dilute acid.** On treating bleachin powder with excess of dilute acid or even carbon dioxide the whol of chlorine present in the molecule is evolved.



$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$
$$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$$

The amount of chlorine thus set free is called "available chlc rine." Bleaching powder is priced according to the amount c available chlorine in the sample. A good sample contains 35·38% of available chlorine.

(*v*) **Decomposition.** In the presence of a little cobalt chlc ride it decomposes to liberate oxygen.



$$2CaOCl_2 \rightarrow 2CaCl_2 + O_2$$

On long standing, it undergoes slow auto-oxidation.



$$6CaOCl_2 \rightarrow Ca(ClO_3)_2 + 5CaCl_2$$

Uses. Bleaching powder is used : (*i*) Chiefly for bleachin cotton, linen and wood pulp in textile and paper factories. Delica articles like straw, silk or ivory are injured by chlorine and ar therefore, bleached with milder bleaching agents like hydroge peroxide and not with bleaching powder.

(*ii*) As a disinfectant and germicide and for sterilization (drinking water.

(*iii*) In rendering wool unshrinkable.

(*iv*) For the manufacture of chloroform.

(*v*) As an oxidising agent in many chemical industries.

7. **Process of Bleaching.**—In big factories bleaching is a automatic process. The article to be bleached, say, a roll of cott cloth, is first boiled with a dilute caustic soda solution. Th removes any grease or wax from the fibres. The strip of cloth then drawn with the help of pulley arrangement, through seve vats as given below :

(*i*) The first vat contains a solution of bleaching powder bleaching solution obtained by electrolysis of cold dilute brine

an undivided cell Some bleaching occurs here probably through the action of atmospheric carbon dioxide which liberates hypochlorous acid, a bleaching agent.

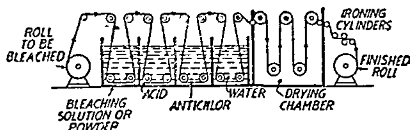


Fig. 34·3—Bleaching of cotton cloth in big factories with bleaching powder or bleaching solution.

(*ii*) The second vat contains a dilute acid solution. The acid liberates chlorine from the bleaching solution and thus completes the bleaching started in the first vat.

(*iii*) The third vat contains the solution of an antichlor, *e.g.*, sodium bisulphite or hypo used to destroy the last traces of chlorine sticking to the fibre. Chlorine injures the fibre, if not destroyed quickly after bleaching is over.



$$NaHSO_3+Cl_2+H_2O \rightarrow NaHSO_4+2HCl$$

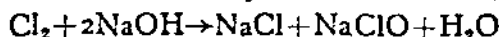
(*iv*) This strip of cloth is next washed thoroughly in the fourth vat containing water It is dried as it passes through the drying cylinders and ironed in the ironing cylinders.

Thus a roll of unbleached cloth is being unwrapped on the left and the bleached cloth after drying and ironing is being wrapped on a roll on the right.

8. **Constitution of Bleaching Powder.**

to be a loose
hlorine is not
l.

(*ii*) Chlorine and sodium hydroxide react as follows :



$$Cl_2+2NaOH \rightarrow NaCl+NaClO+H_2O$$

On the analo
bleaching powder
and calcium hypoc
of both calcium chloride and calcium hypochlorite which is not the case as shown below :

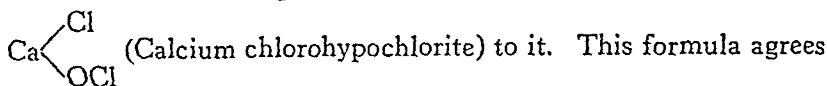
(*a*) Calcium chloride is hygroscopic but bleaching powder is not so.

(*b*) Calcium chloride is soluble in alcohol but no portion of bleaching powder is soluble in alcohol.

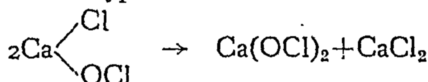
(*c*) Calc 's while
the whole of owder
with excess o

(*d*) Bleaching powder is not obtained by mixing calcium chloride and calcium hypochlorite in equimolecular proportions.

(*iii*) **Odling** suggested in 1861 that it is a mixed salt of hydrochloric acid and hypochlorous acid and assigned the formula



$Ca\langle^{Cl}_{OCl}$ (Calcium chlorohypochlorite) to it. This formula agrees with all its known properties, *e.g.*, percentage of available chlorine and auto-oxidation. In solution it decomposes into calcium chloride and calcium hypochlorite.

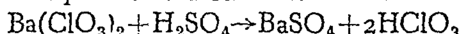


$$2Ca\langle^{Cl}_{OCl} \rightarrow Ca(OCl)_2 + CaCl_2$$

(*iv*) **Bunn, Clark and Clifford** proposed in 1935 that on passing chlorine over slaked lime, basic hypochlorite, $Ca(ClO)_2.2Ca(OH)_2$ and a non-deliquescent basic chloride $CaCl_2.Ca(OH)_2.H_2O$ are the first products of reaction. The basic hypochlorite first produced gives on further chlorination calcium hypochlorite, $Ca(ClO)_2.4H_2O$.

Thus according to them bleaching powder is a mixture of *calcium hypochlorite*, $Ca(ClO)_2.4H_2O$ and *basic calcium chloride* $CaCl_2.Ca(OH)_2.H_2O$.

9. **Chloric acid ($HClO_3$).**—This acid is prepared by the action of dilute sulphuric acid on barium chlorate.

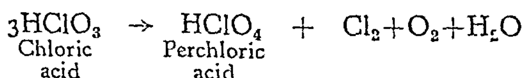


$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2HClO_3$$

Insoluble barium sulphate is filtered off and unused sulphuric acid precipitated with baryta water. The filtrate is evaporated in a vacuum desiccator over concentrated sulphuric acid until a 4 per cent solution of chloric acid is obtained.

Properties. Concentrated chloric acid is colourless, pungent-smelling liquid fairly stable in dark. In light it decomposes and is a powerful oxidizing and bleaching agent. Organic substances, *e.g.*, paper, cotton, wool catch fire in contact with the acid.

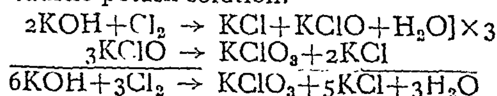
On evaporation or distillation chloric acid undergoes auto-oxidation to give perchloric acid, the most stable oxy-acid of chlorine.



$$\underset{\text{Chloric acid}}{3HClO_3} \rightarrow \underset{\text{Perchloric acid}}{HClO_4} + Cl_2 + O_2 + H_2O$$

10. **Potassium Chlorate.**—This is the most important salt of chloric acid.

Preparation. A sample of potassium chlorate can be prepared in the laboratory by passing chlorine through a boiling concentrated caustic potash solution.

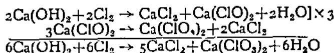


$$[2KOH + Cl_2 \rightarrow KCl + KClO + H_2O] \times 3$$
$$3KClO \rightarrow KClO_3 + 2KCl$$
$$\overline{6KOH + 3Cl_2 \rightarrow KClO_3 + 5KCl + 3H_2O}$$

On concentration and cooling, potassium chlorate crystallizes out.

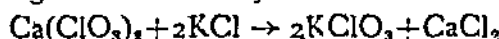
Manufacture. Potassium chlorate is usually prepared on a commercial scale as follows :

(i) **Old Process.** Chlorine is passed through hot milk of lime kept agitated in a cast iron tank when calcium chlorate is produced.



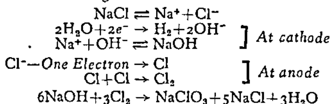
$$2Ca(OH)_2+2Cl_2 \rightarrow CaCl_2+Ca(ClO)_2+2H_2O] \times 3$$
$$3Ca(ClO)_2 \rightarrow Ca(ClO_3)_2+2CaCl_2$$
$$6Ca(OH)_2+6Cl_2 \rightarrow 5CaCl_2+Ca(ClO_3)_2+6H_2O$$

Free lime is allowed to settle and decanted liquor is treated with potassium chloride (equivalent quantity) when potassium chlorate being least soluble crystallizes on cooling



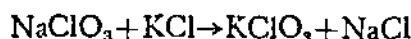
$$Ca(ClO_3)_2+2KCl \rightarrow 2KClO_3+CaCl_2$$

(ii) **Modern Electrolytic Process.** A hot concentrated solution of common salt is electrolysed in an undivided cell. Hydroxyl ions liberated at cathode by reduction of water react with Na^+ to give caustic soda, which reacts hot with chlorine liberated at the anode to give sodium chlorate.



$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$\left.\begin{array}{l} 2H_2O+2e^- \rightarrow H_2+2OH^- \\ Na^+ + OH^- \rightleftharpoons NaOH \end{array}\right] \textit{At cathode}$$
$$\left.\begin{array}{l} Cl^- - \textit{One Electron} \rightarrow Cl \\ Cl+Cl \rightarrow Cl_2 \end{array}\right] \textit{At anode}$$
$$6NaOH+3Cl_2 \rightarrow NaClO_3+5NaCl+3H_2O$$

This is treated with an equivalent amount of potassium chloride when least soluble potassium chlorate crystallizes out on cooling.

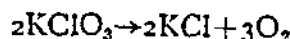


$$NaClO_3+KCl \rightarrow KClO_3+NaCl$$

Electrolysis of potassium chloride will give potassium chlorate direct but this being sparingly soluble, crystallizes during the course of electrolysis and creates trouble Hence it is best to start with sodium chloride as indicated above.

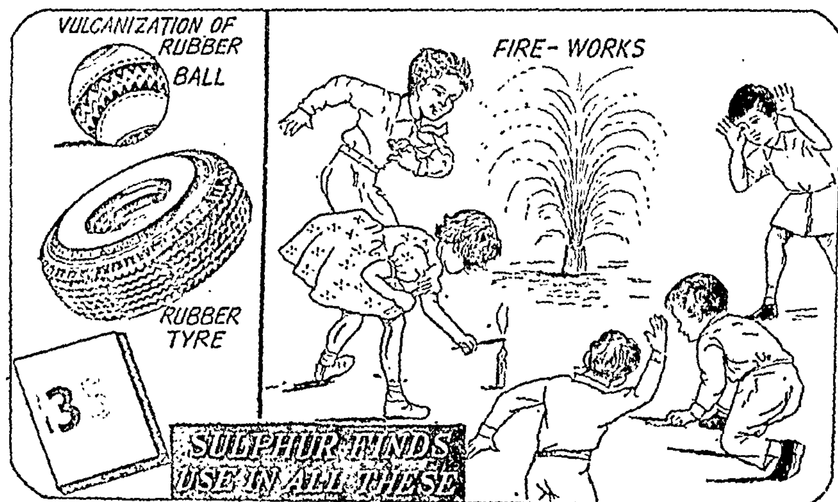
Properties. Potassium chlorate is a white crystalline substance, slightly soluble in water. Its various chemical reactions are :

(i) **Action of Heat.** On heating it decomposes to give oxygen. The decomposition is catalysed by the presence of manganese dioxide.



$$2KClO_3 \rightarrow 2KCl+3O_2$$

On heat... kes place in tw... perchlorate ... ium perchlo... potassium chloride.



Sulphur

1. **Historical.**—Sulphur was known to the ancients probably due to its frequent occurrence in free state. It was used for fumigation and medicine by Aryans, Greeks and Romans while fumes of burning sulphur were used for bleaching. The Bible refers to it as *brimestone* (*burning stone*). The name sulphur is derived from the Sanskrit word '*sulveri*' through the Latin *sulphurium*. Its elementary nature was established by Lavoisier in 1777.

2. **Occurrence.**—Sulphur occurs native, *i.e.*, in the elementary form in the volcanic regions of Sicily, Italy, Japan, South America, Russia and Iceland. Small deposits have been found in Pakistan (Baluchistan) and India (Kangra district in the Himachal). The biggest sulphur deposits of the world are in Louisiana and Texas (U.S.A.). In the combined state sulphur occurs as :

(*i*) **Sulphides**, *e.g.*, zinc blende (ZnS), galena (PbS), copper pyrites ($CuFeS_2$).

(*ii*) **Sulphates**, *e.g.*, Gypsum ($CaSO_4 \cdot 2H_2O$), Barytes ($BaSO_4$) and Epsom salt ($MgSO_4 \cdot 7H_2O$).

(*iii*) Traces of sulphur occur as hydrogen sulphide in volcanic gases. Organic compounds such as eggs, proteins, garlic, onions, mustard, hair and wool contain sulphur.

3. **Extraction of Sulphur.** The two principal world sources of sulphur in Sicily and the States of Louisiana an Texas (America) have their characteristic method for extraction of sulphur called the *Sicilian* and the *Louisiana processes* respectively.

(*i*) **The Sicilian Process.** In Sicily sulphur mixed with clay, limestone and other rocky impurities occurs on the surface and contains about 12—25 per cent of sulphur. It is dug out and piled

up in specially designed kilns called *calcroni* (Fig. 35·1) built on sloping hill-sides, leaving air spaces. The kiln is lighted at the top when some of the sulphur burns and heat produced melts the

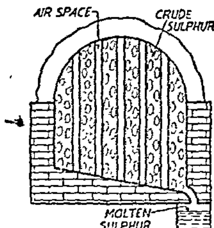


Fig. 35·1—Calcroni

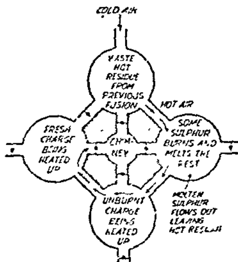


Fig 35·2—Gill's kiln

rest which flows down the slope into a wooden trough below. Molten sulphur is then taken into wooden moulds where it solidifies in the form of blocks.

The method is sufficiently wasteful as about 33 per cent of sulphur is lost during burning.

To save maximum quantity of sulphur, kilns working on *regenerative principle of heat economy* are used. One of such improved type of kilns is the **Gill's Kiln.** In this six closed brick chambers are arranged in a circle with a chimney at the centre. These chambers are connected with one another while each one of them is connected to the chimney and is provided with an independent inlet. Air is heated up as it is blown through the chamber containing waste hot residue and this hot air is used to heat fresh charge in other chambers. Thus no heat is wasted, but still the loss of sulphur is about 20%. This has to be *tolerated* due to shortage of fuel in Sicily.

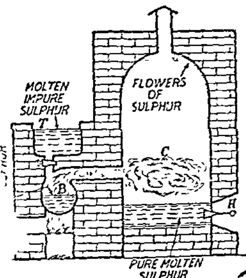


Fig. 35·3—Purification of sulphur by distillation.

Purification of Sulphur. The sulphur obtained above still contains about

5 per cent of earthy impurities. It is used as such or purified by distillation. Purification of Sicilian sulphur is carried out at Marseilles. Crude sulphur is melted and then distilled in large iron retorts connected to a brick chamber (Fig. 35·3). At first, when the walls are cold sulphur vapours condense on the walls to a fine powder called flowers of sulphur and may be removed. Later on as the brick-work heats up to above 120°C, the condensate remains liquid and collects on the floor of the chamber. This liquid is periodically tapped and poured into cylindrical moulds where it solidifies to give *roll-sulphur*.

(2) **The Louisiana or the Frasch Process.** In Louisiana sulphur occurs at a depth of 500—1500 feet and the overlying strata consists of rocks, clay and quicksand. Extraction of sulphur by ordinary mining is impossible, both on account of the difficulties of sinking shafts through water-logged sands, clay and rock strata and the large quantities of hydrogen sulphide and sulphur dioxide which always occur and make it impossible for labourers to work in the shafts sunk. Herman Frasch (1852– 1914), an American chemist, overcame the difficulty by devising the present method known after his name.

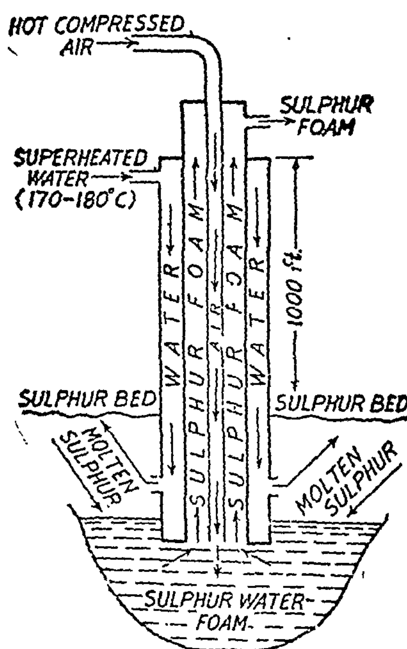
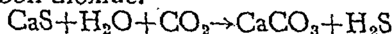


Fig. 35·4—The Louisiana Process of sulphur extraction.

Holes are bored and a 12-inch pipe is driven through the quicksand down to sulphur beds. This pipe serves as the casing (not shown in the figure). Insid the casing are three concentri pipes, 6 inches, 3 inches and inch in diameter respectivel (Fig. 35·4). Superheated wate at 170—180°C is admitted throug the 6-inch pipe while hot air com pressed to about 35 atmosphere is blown down the 1-inch pipe Superheated water melts th sulphur and hot compressed ai blows it into an aerated sulphur water emulsion and then force it up through the 3-inch pipe.

This emulsion flows int large wooden vats where sulphu solidifies. It is about 99·5 pe cent pure and needs no furthe purification. But if it must b further purified for some specia purposes it may be done by dis tillation as given before.

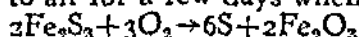
(3) **Sulphur from Waste Products.** (*a*) *From alkali wast obtained as a by-product in the Leblanc Process.* Alkali waste which is mainly calcium sulphide, is suspended in water and treat ed with carbon dioxide.



$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$$

Hydrogen sulphide thus liberated is burnt in an insufficient

(*b*) *From spent oxides of the gas works.* Spent oxides from purifiers used in coal gas plants mainly consist of ferric sulphide. This is exposed to air for a few days when sulphur is deposited.



$$2Fe_2S_3+3O_2 \rightarrow 6S+2Fe_2O_3$$

4. **Properties of Sulphur.**

Physical. (i) Ordinary sulphur is a pale yellow brittle solid crystalline in nature.

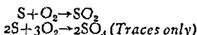
(*ii*) It has a marked taste and a faint odour. It is without physiological action on human beings but poisonous to lower organisms.

(*iii*) It is insoluble in water but readily soluble in carbon disulphide and sparingly soluble in alcohol and ether.

(*iv*) It is a poor conductor of heat and a bad conductor of electricity. It is, therefore, an excellent insulator.

(v) ... forms.

C ... ated to 250°C, ... a little *trioxide as well.*

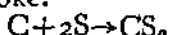


$$S+O_2 \rightarrow SO_2$$

$$2S+3O_2 \rightarrow 2SO_3 \text{ (Traces only)}$$

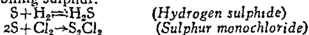
(2) **Combination with elements.** It is as active as oxygen and combines with a number of elements, metals and non-metals. For example,

(*a*) With carbon it combines when sulphur vapours are passed over red hot coke.



$$C+2S \rightarrow CS_2$$

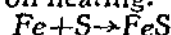
(*b*) With hydrogen and chlorine it combines when the gases are passed through boiling sulphur.



$$S+H_2 \rightleftharpoons H_2S \quad \text{(Hydrogen sulphide)}$$

$$2S+Cl_2 \rightarrow S_2Cl_2 \quad \text{(Sulphur monochloride)}$$

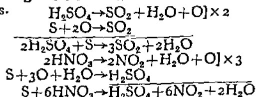
(*c*) With most of the metals such as copper, iron, mercury and zinc, it combines on heating.



$$Fe+S \rightarrow FeS$$

Here it acts as an *oxidizing agent* and oxidizes iron to iron sulphide (FeS).

(3) **Reducing action.** It reduces hot concentrated sulphuric and nitric acids.



$$H_2SO_4 \rightarrow SO_2+H_2O+O] \times 2$$

$$S+2O \rightarrow SO_2$$

$$2H_2SO_4+S \rightarrow 3SO_2+2H_2O$$

$$2HNO_3 \rightarrow 2NO_2+H_2O+O] \times 3$$

$$S+3O+H_2O \rightarrow H_2SO_4$$

$$S+6HNO_3 \rightarrow H_2SO_4+6NO_2+2H_2O$$

(4) **With alkalis.** Sulphur dissolves in alkalis on heating to give sulphides and thiosulphates. The interaction is rather complex and is followed by soultion of sulphur in the sodium sulphide to



$$\ldots +Na_2S_2O_3+3H_2O$$

(5) **With oxidising agents.** Sulphur forms explosive mixtures with oxidising agents, *i.e.*, potassium chlorate, potassium nitrate.

5 per cent of earthy impurities. It is used as such or purified by distillation. Purification of Sicilian sulphur is carried out at Marseilles. Crude sulphur is melted and then distilled in large iron retorts connected to a brick chamber (Fig. 35·3). At first, when the walls are cold sulphur vapours condense on the walls to a fine powder called flowers of sulphur and may be removed. Later on as the brick-work heats up to above 120°C, the condensate remains liquid and collects on the floor of the chamber. This liquid is periodically tapped and poured into cylindrical mould where it solidifies to give *roll-sulphur*.

(2) **The Louisiana or the Frasch Process.** In Louisiar sulphur occurs at a depth of 500—1500 feet and the overlying stra consists of rocks, clay and quicksand. Extraction of sulphur b ordinary mining is impossible, both on account of the difficulties c sinking shafts through water-logged sands, clay and rock strata an the large quantities of hydrogen sulphide and sulphur dioxic which always occur and make it impossible for labourers to wo in the shafts sunk. Herman Frasch (1852– 1914), an America chemist, overcame the difficulty by devising the present methc known after his name.

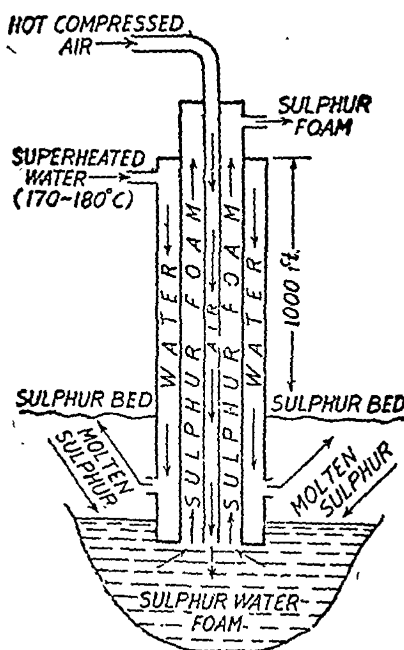


Fig. 35·4—The Louisiana Process of sulphur extraction.

Holes are bored and a 12-inc pipe is driven through th quicksand down to sulphur bed This pipe serves as the casin (not shown in the figure). Insic the casing are three concentr pipes, 6 inches, 3 inches and inch in diameter respectivel (Fig. 35·4). Superheated wate at 170—180°C is admitted throug the 6-inch pipe while hot air com pressed to about 35 atmosphere is blown down the 1-inch pip Superheated water melts th sulphur and hot compressed a blows it into an aerated sulphu water emulsion and then force it up through the 3-inch pipe.

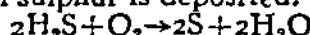
This emulsion flows int large wooden vats where sulphu solidifies. It is about 99·5 pe cent pure and needs no furthe purification. But if it must b further purified for some speci purposes it may be done by di tillation as given before.

(3) **Sulphur from Waste Products.** (*a*) *From alkali wast obtained as a by-product in the Leblanc Process.* Alkali wast which is mainly calcium sulphide, is suspended in water and treat ed with carbon dioxide.



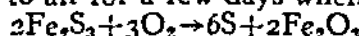
$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$$

Hydrogen sulphide thus liberated is burnt in an insufficient supply of air when sulphur is deposited.



$$2H_2S+O_2 \rightarrow 2S+2H_2O$$

(*b*) *From spent oxides of the gas works.* Spent oxides from purifiers used in coal gas plants mainly consist of ferric sulphide. This is exposed to air for a few days when sulphur is deposited.



$$2Fe_2S_3+3O_2 \rightarrow 6S+2Fe_2O_3$$

4. **Properties of Sulphur.**

Physical. (*i*) Ordinary sulphur is a pale yellow brittle solid crystalline in nature.

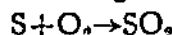
(*ii*) It has a marked taste and a faint odour. It is without physiological action on human beings but poisonous to lower organisms.

(*iii*) It is insoluble in water but readily soluble in carbon disulphide and sparingly soluble in alcohol and ether.

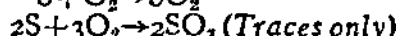
(*iv*) It is a poor conductor of heat and a bad conductor of electricity. It is, therefore, an excellent insulator.

(*v*) It exhibits allotropy and exists in several allotropic forms.

Chemical (1) **Burning.** It burns in air, when heated to 250°C, with a pale blue flame giving sulphur dioxide and a little trioxide as well.



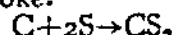
$$S+O_2 \rightarrow SO_2$$



$$2S+3O_2 \rightarrow 2SO_3 \text{ (Traces only)}$$

(2) **Combination with elements.** It is as active as oxygen l combines with a number of elements, metals and non-metals. r example,

(*a*) With carbon it combines when sulphur vapours are ssed over red hot coke.

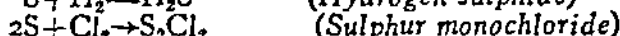


$$C+2S \rightarrow CS_2$$

(*b*) With hydrogen and chlorine it combines when the gases : passed through boiling sulphur.

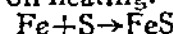


$$S+H_2 \rightleftharpoons H_2S \quad \text{(Hydrogen sulphide)}$$



$$2S+Cl_2 \rightarrow S_2Cl_2 \quad \text{(Sulphur monochloride)}$$

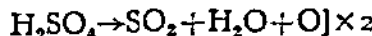
(*c*) With most of the metals such as copper, iron, mercury l zinc, it combines on heating.



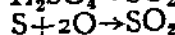
$$Fe+S \rightarrow FeS$$

Here it acts as an *oxidizing agent* and oxidizes iron to iron phide (FeS).

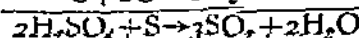
(3) **Reducing action.** It reduces hot concentrated sulphuric d nitric acids.



$$H_2SO_4 \rightarrow SO_2+H_2O+O] \times 2$$



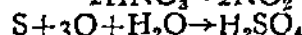
$$S+2O \rightarrow SO_2$$



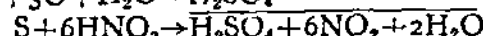
$$2H_2SO_4+S \rightarrow 3SO_2+2H_2O$$



$$2HNO_3 \rightarrow 2NO_2+H_2O+O] \times 3$$

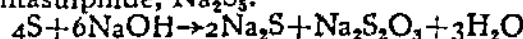


$$S+3O+H_2O \rightarrow H_2SO_4$$

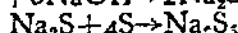


$$S+6HNO_3 \rightarrow H_2SO_4+6NO_2+2H_2O$$

(4) **With alkalis.** Sulphur dissolves in alkalis on heating to re sulphides and thiosulphates. The interaction is rather complex d is followed by soultion of sulphur in the sodium sulphide to rm sodium pentasulphide, Na_2S_5.



$$4S+6NaOH \rightarrow 2Na_2S+Na_2S_2O_3+3H_2O$$



$$Na_2S+4S \rightarrow Na_2S_5$$

(5) **With oxidising agents.** Sulphur forms explosive mixtures ith oxidising agents, *i.e.*, potassium chlorate, potassium nitrate.

5. **Uses of Sulphur.**—(1) Large quantities of sulphur are used in the manufacture of :

(*i*) Sulphur dioxide used for fumigation, bleaching andneeded for the manufacture of sulphuric acid, sulphites and thiosulphates

(*ii*) Sulphur compounds like carbon disulphide and phosphorus trisulphide, P_4S_3 are extensively used in match industry.

(*iii*) Gun-powder (a mixture of sulphur, charcoal and potassium nitrate) and fireworks.

(*iv*) Calcium bisulphite needed in paper industry.

(2) *In agriculture.* Sulphur alone or mixture of sulphur with lead arsenate or lime is used as fungicide.

(3) *In medicine.* Sulphur is used internally or as sulphur ointment in skin eruptions.

(4) *In Vulcanization of Rubber.* Vulcanization is the heating of the rubber mixture (with sulphur as one of the ingredients) to a definite temperature for a definite time. It removes the sticky qualities of rubber, makes it more elastic and gives the articles produced a permanent shape.

(5) *In the manufacture of Sulphur dyes.* Sulphur dyes are used for dyeing hosiery.

6. **Effect of Heat on Sulphur.**—Ordinary sulphur melts on heating at 114·5°C to a pale yellow mobile liquid. On heating further instead of becoming more mobile, as liquids usually do, it grows thicker and more viscous. At the same time the colour changes from a light yellow to reddish brown and then to almost black. At about 180°C the mass becomes so viscous that it cannot be poured out by inverting the test tube. Viscosity goes on decreasing above 180°C till at445°C it flows freely and begins to boil giving heavy red vapour corresponding to formula S_8. The vapours on heating dissociate to S_4, S_2 till finally at 2000°C, vapour density corresponds to the formula S. *These changes are reversed on cooling.* This unusual behaviour of sulphur is explained as follows :

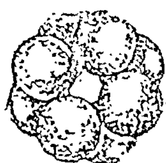


Fig. 35·6—A model of sulphur molecules, S_8.

The sulphur molecule, consists of a ring of eight atoms (Fig. 35·6). The ring tends to break up on heating and chains of sulphur atoms are produced. When sulphur melts, the S_8 rings slip and roll over one another easily (not viscous). When (liquid sulphur is heated, the rings are broken into chains which then join, forming very long molecules (Fig. 35·7). These long molecules become entangled with one another (*very viscous*). When the temperature rises beyond 200°, these chains break up more and more, and viscosity goes on decreasing with rise of temperature.

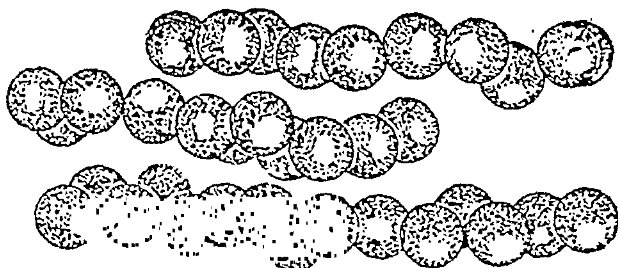


Fig. 35·7—Model representing the sulphur atoms formed in molten sulphur by the breaking and joining of S_8 molecules.

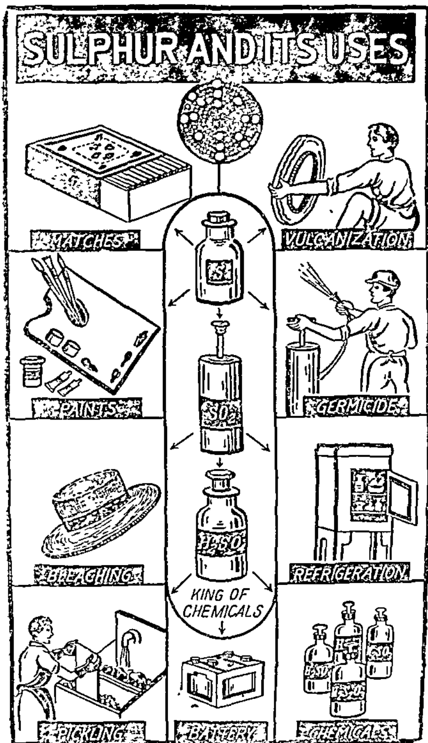

SULPHUR AND ITS USES
MATCHES
VULCANIZATION
S
PAINTS
SO_2
GERMICIDE
BLEACHING
H_2SO_4
REFRIGERATION
KING OF CHEMICALS
PICKLING
BATTERY
CHEMICALS

Fig. 35 5

7. Allotropic Modifications of Sulphur.—Sulphur exhibits allotropy and exists in several solid allotropic forms. These differ *somewhat in physical* properties and in the manner in which they are produced as given below :

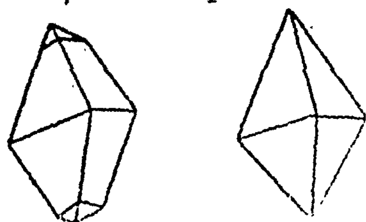


Fig. 35·8—Rhombic crystals of α-sulphur.

(*i*) **Rhombic, Octahedral or α-Sulphur** (m.p. 112·8°C and sp. gr. 2·06). This is the variety stable at ordinary temperature.

All other varieties gradually change into this form on standing. It is prepared by evaporating solution of roll sulphur in carbon disulphide when rhombic or octahedral crystals of α-sulphur (Fig. 35·8) are obtained. It is soluble in carbon disulphide.

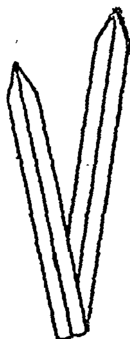


Fig 35·9—Monoclinic crystals of β-sulphur.

(*ii*) **Monoclinic, Prismatic or β-sulphur** (*m.p. 112·2°C and sp. gr. 1·98*). This variety is prepared by melting sulphur in a dish and cooling till crust is formed. Two holes are made in the crust and liquid poured out. On removing the crust, colourless needle shaped crystals of β-sulphur (Fig. 35·9) are seen. It is stable above 96°C and passes into α-sulphur below it. Conversely α-sulphur is stable below 96°C and passes into β-sulphur above this. At 96°C both the forms are stable. This temperature is called *transition temperature* and two varieties are called *enantiotropic* substances. It is soluble in carbon disulphide.

(*iii*) **Plastic Sulphur or γ-sulphur** (sp. gr. 1·95). Plastic sulphur is obtained by pouring boiling sulphur in cold water when rubber-like mass is obtained (Fig. 35·10). It is insoluble in carbon disulphide. The rubber-like mass is a supercooled liquid and as such has no sharp melting point. It is unstable and passes into the rhombic variety on standing.

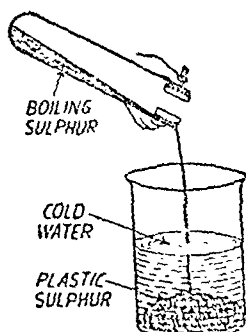
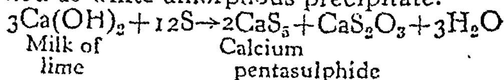
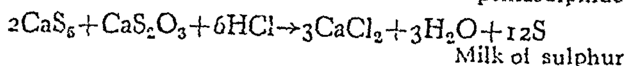


Fig. 35·10—Plastic sulphur.

(*iv*) **Milk of sulphur.** This variety of sulphur is obtained by boiling milk of lime with sulphur and decomposing the calcium pentasulphide thus formed with hydrochloric acid when milk of sulphur is precipitated as white amorphous precipitate.



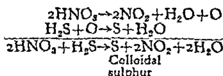
$$\underset{\text{Milk of lime}}{3Ca(OH)_2} + 12S \rightarrow \underset{\text{Calcium pentasulphide}}{2CaS_5} + CaS_2O_3 + 3H_2O$$



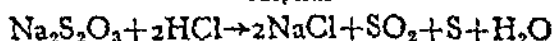
$$2CaS_5 + CaS_2O_3 + 6HCl \rightarrow 3CaCl_2 + 3H_2O + \underset{\text{Milk of sulphur}}{12S}$$

Milk of sulphur is soluble in carbon *disulphide and is used* largely in medicine.

(*v*) **Colloidal sulphur.** Sulphur is precipitated in the colloidal form when hydrogen sulphide is bubbled through nitric acid or when sodium thiosulphate solution is treated with dilute hydrochloric acid.



$$2HNO_3 \rightarrow 2NO_2 + H_2O + O$$
$$H_2S + O \rightarrow S + H_2O$$
$$2HNO_3 + H_2S \rightarrow \underset{\text{Colloidal sulphur}}{S} + 2NO_2 + 2H_2O$$



$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$$

One heating or long standing, colloidal sulphur changes into the ordinary form.

The relationship of the various allotropes of sulphur is summarized in the following chart :

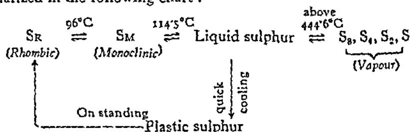


Fig. 35·11—Various allotropes of Sulphur.

8. **Proof that these forms of sulphur are the allotropic forms of the same element.**—Different forms of sulphur are chemically identical. For example, a known weight of any of these forms on burning produces the same quantity of sulphur dioxide. This proves that these are allotropic modifications of the same e

2. How does sulphur occur in nature? How is it extracted by tl Sicilian or the Frasch Process?

Name the various allotropic forms of sulphur and prove their chemic identity. How are they distinguished from one another? How does sulph react with sulphuric acid and carbon? *(Delhi H.S. 196*

3. Describe in brief outline the process used for obtaining sulph from its underground deposits. Explain why the hot water used in this oper tion is heated under pressure? With what object is the air blown in tl mixture of molten sulphur and water? Why is the sulphur so obtained. much as 99·5% pure?

How would you convert it into (*a*) hydrogen sulphide, (*b*) sodium su phite, and (*c*) sulphuric acid. *(Delhi H.S. 1969, 6*

4. Write a short note on 'Allotropic forms of sulphur'.
(Punjab Pre-University 1969, 6

5. Describe the physical changes through which sulphur passes whe heated in the absence of air. What are the principal uses of sulphur?

6. Starting with roll sulphur, how will you prepare sulphur dioxid hydrogen sulphide and sulphur trioxide respectively? What is the action each of these compounds on water and acidified solution of potassium pe manganate?

7. Give the preparation, properties and uses of colloidal sulphur.

Test Your Understanding

8. Fill in the blanks :

(*a*) A sulphur molecule contains......atoms arranged......

(*b*) Sulphur obtained......is quite pure and does not require furth purification.

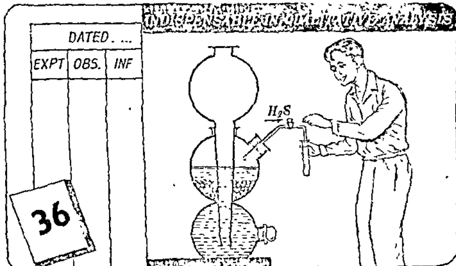
(*c*) Sulphur dissolves in boiling NaOH due to the formation of......

(*d*) Sulphur......nitric acid to oxides of nitrogen and itself is......to......

(*e*) If α-sulphur is kept above 96°C it slowly passes into......

KEY

8. (*a*) 8 ; in a puckered ring ; (*b*) by Frasch process ; (*c*) $Na_2S_2O_3$ an Na_2S_x ; (*d*) reduces ; oxidized ; H_2SO_4 (*e*) β-sulphur.

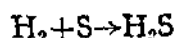


Hydrogen Sulphide

1. **Historical.**—Hydrogen sulphide or sulphuretted hydro- [illegible] chemists of the Middle Ages [illegible] ". It was systematically in- [illegible] 1777.

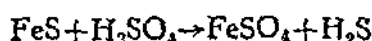
2. **Occurrence.**—Hydrogen sulphide is found in natural gas, coal gas and cracked hydrocarbons. Many mineral springs owe their odour and taste to its presence. It occurs wherever animal or vegetable matter decays in a limited supply of air.

3. **Preparation.**—(i) The gas may be prepared by direct union of hydrogen and sulphur by passing hydrogen gas through boiling sulphur.



$$H_2 + S \rightarrow H_2S$$

(ii) **Laboratory Method.** Hydrogen sulphide is prepared in the laboratory by the action of dilute hydrochloric acid or sulphuric acid on iron sulphide.



$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

Iron sulphide is taken in a Woulfe's bottle fitted with a thistle funnel and a delivery tube twice bent at right angles (Fig. 36·1). Dilute acid is poured through the thistle funnel and the gas is collected by an upward displacement of air.

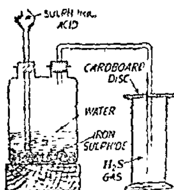
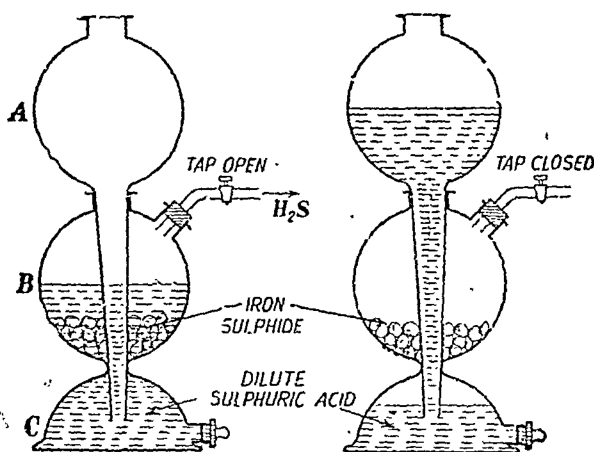


Fig. 36·1—Preparation of hydrogen sulphide in the laboratory.

Since hydrogen sulphide is frequently required in the laboratory for qualitative analysis, it is prepared in a Kipp's apparatus (Fig. 36·2). It consists of a bulb *A* with a long-stem fitting into the neck of the *base* (made of two bulbs *B* and *C*) and reaching the bottom of bulb *C*.

Iron sulphide is placed in the bulb *B* and dilute sulphuric acid is poured in *A* from where it fills the bulb *C* and rises in the bulb *B*. Here it comes in contact with iron sulphide and liberates hydrogen sulphide which exerts pressure and pushes sulphuric acid back into the bulbs *C* and *A*. Thus further reaction stops. Whenever gas is needed, it is taken out through the tap provided. The gas having escaped, the pressure in the bulb *B* falls and sulphuric acid again rises in it to produce more gas and fill it with the gas.

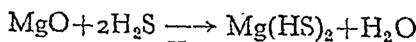
Purification. Hydrogen sulphide so prepared contains some acid spray in addition to traces of hydrogen produced by the action of acid on iron present as impurity. Hydrogen does not interfere with its reactions and need not be removed. Acid spray is removed ordinarily by bubbling the gas through water. It can, however, be better purified by absorbing the gas in magnesium oxide suspension in water and heating it later to 60°C.



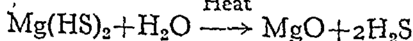
(a) After the gas is taken out acid rises in the bulb *B* to produce more gas.

(b) After closing the stop-cock the bulb *B* is full of gas and further reaction stops.

Fig. 36·2—Kipp's apparatus.

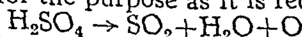


$$MgO + 2H_2S \longrightarrow Mg(HS)_2 + H_2O$$

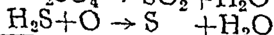


$$Mg(HS)_2 + H_2O \xrightarrow{\text{Heat}} MgO + 2H_2S$$

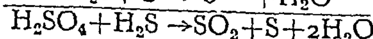
Drying. It is dried by passing the moist gas through calcium chloride or phosphorus pentoxide. Concentrated sulphuric acid cannot be employed for the purpose as it is reduced by the gas.



$$H_2SO_4 \rightarrow SO_2 + H_2O + O$$

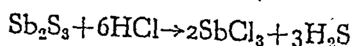


$$H_2S + O \rightarrow S + H_2O$$



$$H_2SO_4 + H_2S \rightarrow SO_2 + S + 2H_2O$$

(*iii*) **Pure gas.** Pure hydrogen sulphide is obtained by heating powdered antimony sulphide with pure concentrated hydrochloric acid.



$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S$$

4. Properties of Hydrogen Sulphide.

Physical (*i*) Hydrogen sulphide is a colourless gas with an offensive odour resembling that of rotten eggs.

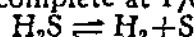
(*ii*) It is slightly heavier than air.

(*iii*) It is fairly soluble in water and the solution smells like the gas.

(*iv*) It is extremely poisonous in nature. When inhaled in small amounts, it produces severe headache whereas larger amounts cause death.

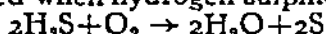
(*v*) It can be easily condensed to a liquid (b.p. = −60°C and f.p. = −83°C).

Chemical. (1) **Thermal dissociation.** Hydrogen sulphide decomposes, when heated, into hydrogen and sulphur. Dissociation begins at 310°C and is complete at 1700°C.

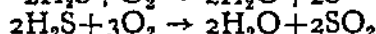


$$H_2S \rightleftharpoons H_2 + S$$

(2) **Combustibility.** It is combustible and burns with a blue flame giving sulphur in limited supply of air whereas sulphur dioxide is produced when hydrogen sulphide burns in excess of air.

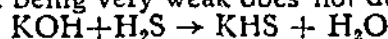


$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$



$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

(3) **Acid Properties.** The aqueous solution of hydrogen sulphide behaves as a typical weak dibasic acid (Hydrosulphuric acid). *It gives two series of salts* with alkalis, acid and normal salts. The acid being very weak does not decompose carbonates.

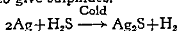


$$KOH + H_2S \rightarrow \underset{\text{(Acid salt)}}{KHS} + H_2O$$

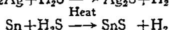


$$2KOH + H_2S \rightarrow \underset{\text{(Normal salt)}}{K_2S} + 2H_2O$$

(4) **Action on Metals.** It reacts with numerous metals, *e.g.*, silver, tin zinc, to give sulphides.



$$2Ag + H_2S \xrightarrow{\text{Cold}} Ag_2S + H_2$$

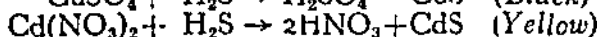


$$Sn + H_2S \xrightarrow{\text{Heat}} SnS + H_2$$

(5) **Precipitation of Metal sulphides.** It reacts with many metallic salts precipitating sulphides with characteristic colours.



$$CuSO_4 + H_2S \rightarrow H_2SO_4 \quad CuS \quad (\textit{Black})$$



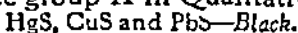
$$Cd(NO_3)_2 + H_2S \rightarrow 2HNO_3 + CdS \quad (\textit{Yellow})$$



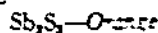
$$2SbCl_3 + 3H_2S \rightarrow 6HCl + Sb_2S_3 \quad (\textit{Orange})$$

Its use as an Analytical reagent. Its utility in analytical chemistry lies in its above property of precipitation of a number of sulphides with characteristic colours from metallic salts. The colour of the ppt. coupled with the information whether obtained in acidic or in alkaline solution gives a clue to the identity of the basic radical.

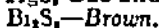
(*a*) The sulphides which are precipitated in acidic solution and constitute group II in Qualitative Analysis are :



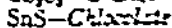
HgS, CuS and PbS—*Black*.



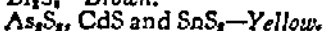
Sb_2S_3—*Orange*



Bi_2S_3—*Brown*.



SnS—*Chocolate*



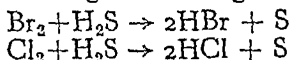
As_2S_3, CdS and SnS_2—*Yellow*.

(*b*) The sulphides which are precipitated in ammoniacal solution containing ammonium chloride and constitute group IV in Qualitative Analysis are :

CoS and NiS—*Black*. ZnS—*White*
MnS—*Flesh coloured*.

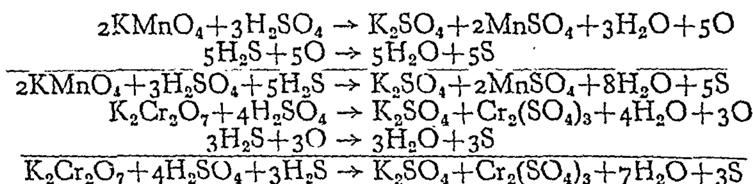
(6) **Reducing Property.** Due to the ease with which it can liberate nascent hydrogen ($H_2S \rightarrow S+2H$) or take up an atom of oxygen ($H_2S+O \rightarrow S+H_2O$), hydrogen sulphide acts as an active reducing agent.

(*i*) It reduces halogens to halogen acids.



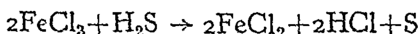
$$Br_2+H_2S \rightarrow 2HBr + S$$
$$Cl_2+H_2S \rightarrow 2HCl + S$$

(*ii*) It decolorises acidified potassium permanganate solution while potassium dichromate solution (*acidified*) is turned green.



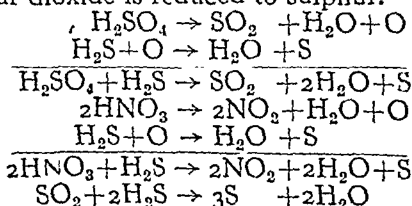
$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5O$$
$$5H_2S+5O \rightarrow 5H_2O+5S$$
$$\overline{2KMnO_4+3H_2SO_4+5H_2S \rightarrow K_2SO_4+2MnSO_4+8H_2O+5S}$$
$$K_2Cr_2O_7+4H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O$$
$$3H_2S+3O \rightarrow 3H_2O+3S$$
$$\overline{K_2Cr_2O_7+4H_2SO_4+3H_2S \rightarrow K_2SO_4+Cr_2(SO_4)_3+7H_2O+3S}$$

(*iii*) Ferric salts are reduced to ferrous salts by hydrogen sulphide.



$$2FeCl_3+H_2S \rightarrow 2FeCl_2+2HCl+S$$

(*iv*) It reduces sulphuric acid to sulphur dioxide, nitric acid to nitrogen dioxide while sulphur dioxide is reduced to sulphur.



$$H_2SO_4 \rightarrow SO_2 + H_2O+O$$
$$H_2S+O \rightarrow H_2O + S$$
$$\overline{H_2SO_4+H_2S \rightarrow SO_2 + 2H_2O+S}$$
$$2HNO_3 \rightarrow 2NO_2+H_2O+O$$
$$H_2S+O \rightarrow H_2O + S$$
$$\overline{2HNO_3+H_2S \rightarrow 2NO_2+2H_2O+S}$$
$$SO_2+2H_2S \rightarrow 3S + 2H_2O$$

(7) **Formation of Poly-sulphides.** On passing excess of hydrogen sulphide through ammonium sulphide, we get yellow ammonium sulphide [ammonium poly-sulphide, $(NH_4)_2S_x$]. Similarly calcium poly-sulphide is obtained by passing hydrogen sulphide (*excess*) through calcium sulphide.

5. **Uses.**—Hydrogen sulphide is an important laboratory reagent. Its use as an analytical reagent has been explained. It is also used as a reducing agent and for the preparation of metallic sulphides many of which find use as paint pigments.

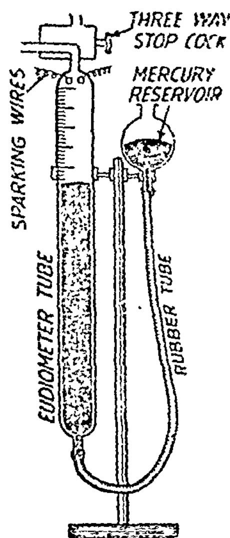


Fig. 36·3—Decomposition of hydrogen sulphide by sparking.

6. **Tests for Hydrogen Sulphide.**—It may be recognised by—

(*i*) *Its offensive rotten eggs' smell.*

(*ii*) Its ability to darken lead acetate paper.

(*iii*) Its property of giving beautiful violet colour with ammoniacal solution of sodium nitroprusside.

7. **Composition.**—(*i*) Hydrogen sulphide is formed when hydrogen is passed through boiling sulphur. It decomposes into hydrogen and sulphur on heating or passing electric sparks through it. *This shows that it is made of hydrogen andsulphur atoms only.*

(*ii*) A known ... over mercury in a eudior... *sparks between sparl...* hydrogen and sulphu... is found to have remained unchanged, showing thereby that *hydrogen sulphide leaves its own volume of hydrogen on decomposition.*

An alternative method to arrive at the same result is as follows :

A known volume of hydrogen sulphide is enclosed over mercury in a graduated bent tube (Fig. 36·4) containing some tin foil in the bent portion. The bent portion of the tube is heated when tin sulphide is formed and hydrogen gas is liberated. On cooling no change in volume is found, showing thereby that *hydrogen sulphide leaves its own volume of hydrogen on decomposition.*

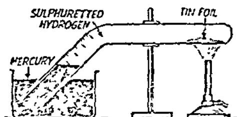
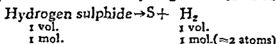


Fig. 36·4—Composition of hydrogen sulphide.

(*iii*) In other words, one volume of hydrogen sulphide on decomposition gives one volume of hydrogen and some sulphur.



$$\text{Hydrogen sulphide} \rightarrow S + H_2$$

1 vol.   1 vol.
1 mol.   1 mol.(=2 atoms)

... hypothesis, we have that one molecule ... and say *x atoms* ...

Vapour density of the gas by experiment $=17$

$\therefore$ Its mol. wt. as calculated from V.D. data $=17\times2=34$

Its mol. wt. from formula $H_2S_x=2+32x$

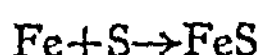
Equating the two molecular weights, we get

$2+32x=34$ whence $x=1.$

$\therefore$ Molecular formula of the gas is H_2S.

8. **Sulphides.**—Salts of hydrosulphuric acid are called sulphides. These may be obtained—

(i) By direct union of the elements, *e.g.*, ferrous sulphide, copper sulphide, carbon disulphide.

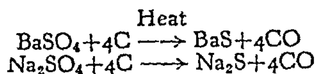


$$Fe + S \rightarrow FeS$$

(ii) By neutralization of alkalis with hydrogen sulphide (*see* page 2·125).

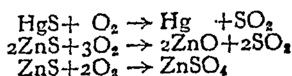
(iii) By precipitation of insoluble sulphides from soluble salts of metals with hydrogen sulphide (*see* page 2·125).

(iv) By reduction of sulphates, *e.g.*, barium sulphate, sodium sulphate with carbon.



$$BaSO_4 + 4C \xrightarrow{\text{Heat}} BaS + 4CO$$
$$Na_2SO_4 + 4C \longrightarrow Na_2S + 4CO$$

General Reactions. (1) **Solubility.** Alkali metal sulphides gives out sulphur dioxide, metal or metal oxide being left behind. In a few cases sulphates are also obtained.



$$HgS + O_2 \rightarrow Hg + SO_2$$
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
$$ZnS + 2O_2 \rightarrow ZnSO_4$$

(2) **With dilute acid.** Sulphides are decomposed with the liberation of hydrogen sulphide when treated with dilute hydrochloric or sulphuric acid.

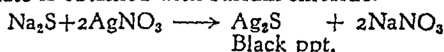


$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

(3) **With oxidizing agents.** Sulphides reduce various oxidizing agents. For example, they decolorise acidified potassium permanganate or bromine water.

(4) **With sodium nitroprusside.** Sodium sulphides give a beautiful violet colour with sodium nitroprusside. This is used as a test for sulphides. To test insoluble sulphides these are first boiled with sodium carbonate to convert them into soluble sodium sulphide.

(5) **With silver nitrate and barium chloride.** Soluble sulphides give a black precipitate of silver sulphide when treated with silver nitrate solution whereas no precipitate is obtained with barium chloride.



$$Na_2S + 2AgNO_3 \longrightarrow \underset{\text{Black ppt.}}{Ag_2S} + 2NaNO_3$$

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Ferrous sulphide+Sulphuric acid.
2. Antimony sulphide+Hydrochloric acid.
3. Hydrogen sulphide+(*i*) Magnesium oxide, (*ii*) Sulphuric acid, (*iii*) Caustic potash, (*iv*) Tin, (*v*) Silver, (*vi*) Chlorine, (*vii*) Potassium permanganate, (*viii*) Potassium dichromate, (*ix*) Nitric acid, and (*x*) Sulphur dioxide.
4. Burning of hydrogen sulphide (*i*) in excess of air, (*ii*) in limited supply of air.
5. Barium sulphate+Carbon (heat).

QUESTIONS

Essay-type Questions

1. How is hydrogen sulphide prepared in the laboratory ? To what use is it put in qualitative analysis in the II and IV groups ? Establish the formula of hydrogen sulphide. (*Bihar H. S. 1961 ; Nagpur Pre-Univ. 1971*)

2. Describe with a neat sketch the preparation and collection of dry hydrogen sulphide. How does this gas react with (*a*) Sodium hydroxide, (*b*) Copper sulphate, (*c*) Ferric chloride, (*d*) Sulphur dioxide, (*e*) Bromine, and (*f*) Cobalt nitrate solution ? (*All India H.S. 1969, 66 ; Delhi 1970*)

3. How is hydrogen sulphide prepared in the laboratory? Give a neat sketch of the apparatus. How can the pure sample of the gas be obtained? How does it react with—

(i) Acidified solution of copper sulphate and mercuric chloride;

(ii) Alkaline solution of zinc chloride and manganous sulphide;

(iii) Aqueous solution of caustic soda;

(iv) Iodine solution; (v) Acidified potassium permanganate solution;

(vi) Sulphurous acid; (vii) Nitric acid,

(viii) Chlorine water; (ix) Silver;

(x) Acidified potassium dichromate solution. (*Delhi H S. 1967, 65, 61*)

4. How is hydrogen sulphide prepared using Kipp's apparatus? How can the gas be dried? What is its use as a reagent in Qualitative Analysis?

Establish the formula of hydrogen sulphide. (*U.P. Board Inter. 1964*)

5 (*a*) Explain why dilute sulphuric acid rather than nitric acid is used in Kipp's apparatus for generating H_2S in the laboratory?

(*b*) How would you obtain sulphur from hydrogen sulphide and *vice versa*?

Test Your Understanding

6. Fill in the blanks:

(*a*) For an intermittent supply of H_2S. ...is used.

(*b*) Incomplete combustion of H_2S produces . ....

(*c*) If H_2S is passed through acidified $K_2Cr_2O_7$ . .....

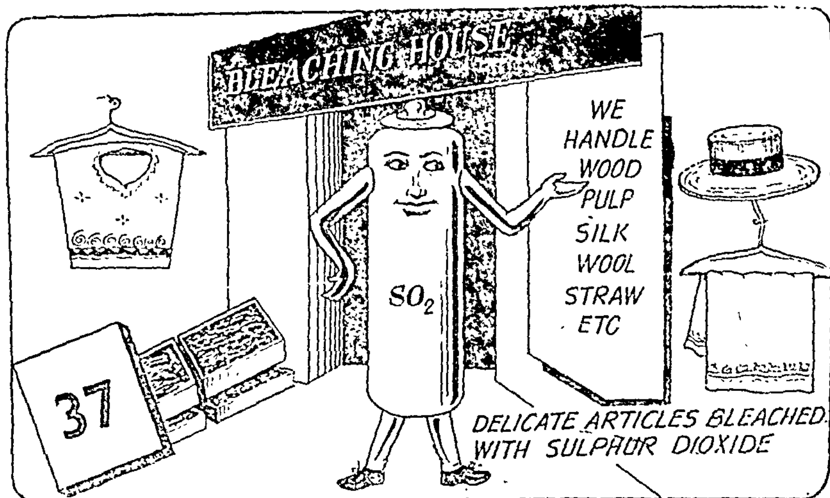
(*d*) Sulphides of group IIA in qualitative analysis can be distinguished from sulphides of IIB . ..

(*e*) CoS is not precipitated from . .solutions while HgS is precipitated.

(*f*) Black precipitates of sulphides encountered during qualitative analysis are those of.. . , . .., ..., ... and.. ...

KEY

6 (*a*) Kipp's apparatus, (*b*) S and H_2O, (*c*) the solution turns green; (*d*) by their insolubility in yellow ammonium sulphide, (*e*) acidic, (*f*) HgS, PbS; CuS, Bi_2S_3; CoS; NiS.



Oxides of Sulphur

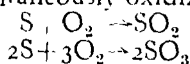
SULPHUR DIOXIDE, SO_2

1. **Historical.**—The use of sulphur dioxide for fumigation has been known since very early times. Priestley prepared the gas by the action of hot concentrated sulphuric acid on mercury in 1770 and called it sulphurous acid.

2. **Occurrence.**—Sulphnr dioxide occurs in volcanic gases and in the springs of volcanic districts. Traces of sulphur dioxide in the town atmosphere are derived from burning of sulphur compounds in coal.

3. **Preparation of Sulphur Dioxide.**—Several ways employed to prepare this gas are :

(*i*) *By burning sulphur in air.* This is the method used for preparing sulphur dioxide on a large scale. About 6—8% of sulphur is simultaneously oxidized to sulphur trioxide.



$$S + O_2 \rightarrow SO_2$$
$$2S + 3O_2 \rightarrow 2SO_3$$

(*ii*) *By roasting sulphides*, e.g., zinc sulphide, iron pyrites. This method is also the one used for preparing large volumes of sulphur dioxide needed in industry, *i.e.*, in the manufacture of sulphuric acid.



$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

(*iii*) *By the reduction of sulphuric acid.* Hot concentrated sulphuric acid is an oxidizing agent. It is reduced to sulphur dioxide when heated with sulphur, copper, mercury, etc. Copper is usually used for the purpose *in the laboratory*

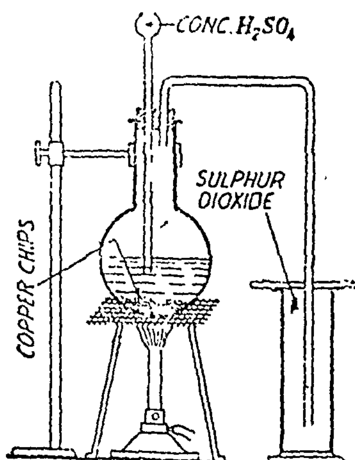
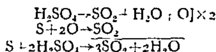
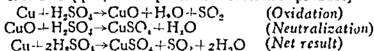


Fig. 37·1 - Laboratory preparation of sulphur dioxide.



$$[H_2SO_4 \rightarrow SO_2 + H_2O + O] \times 2$$
$$S + 2O \rightarrow SO_2$$
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

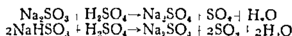
In the case of copper, the sequence of reaction is probably—



$$Cu + H_2SO_4 \rightarrow CuO + H_2O + SO_2 \quad \textit{(Oxidation)}$$
$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \quad \textit{(Neutralization)}$$
$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O \quad \textit{(Net result)}$$

Expt. Take some copper chips in a round-bottom flask fitted with a thistle funnel and a delivery tube twice bent at right angles (Fig 37·1) Pour concentrated sulphuric acid through the thistle funnel and heat the flask. Collect the sulphur dioxide evolved by an upward displacement of air.

(ii) *By the decomposition of sulphites or bisulphites.* Pure sulphur dioxide may be prepared *in the laborotory* by the action of moderately concentrated sulphuric acid on sulphites or bisulphites.



$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + H_2O$$
$$2NaHSO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2SO_2 + 2H_2O$$

Sulphurous acid, H_2SO_3 is first formed. It then decomposes into sulphur dioxide and water

Sodium sulphite is taken in a Woulfe's bottle fitted with a thistle funnel and a delivery tube twice bent at right angles (Fig 36·1 page 2·123) Moderately concentrated sulphuric acid is poured through the thistle funnel and sulphur dioxide is collected as above

4. Properties of Sulphur Dioxide.

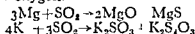
(*a*) Physical. (i) Sulphur dioxide is a colourless gas with a pungent smell of burning sulphur It is poisonous in nature and causes inflammation of the lungs and induces asthmatical complaints.

(ii) It is 2·2 times as heavy as air.

(iii) It is very soluble in water The solution of sulphur dioxide in water is called sulphurous acid.

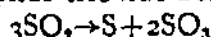
(iv) It is one of the easiest gases to liquefy, since it condenses at room temperature under a pressure of two atmospheres. Liquid sulphur dioxide (b p − 10°C) is sold in the market in steel containers and can be solidified to a snow-like solid (m.p. −76°C).

(*b*) **Chemical (1) Incombustible and Non supporter of Combustion.** Sulphur dioxide is incombustible and a non-supporter of combustion ordinarily. Strongly burning potassium or magnesium, however, continues to burn in a jar of the gas, presumably the heat of the reaction is enough to dissociate the gas into sulphur and free oxygen.



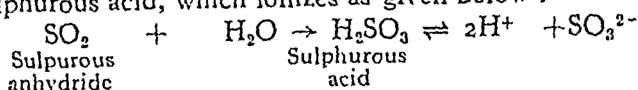
$$3Mg + SO_2 \rightarrow 2MgO + MgS$$
$$4K + 3SO_2 \rightarrow K_2SO_3 + K_2S_2O_3$$

(2) **Thermal Dissociation.** It dissociates when heated strongly, sulphur and sulphur trioxide being formed.



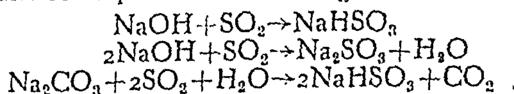
$$3SO_2 \rightarrow S + 2SO_3$$

(3) **Acidic Nature.** Sulphur dioxide dissolves in water to give sulphurous acid, which ionizes as given below :



$$\underset{\text{Sulpurous anhydride}}{SO_2} + H_2O \rightarrow \underset{\text{Sulphurous acid}}{H_2SO_3} \rightleftharpoons 2H^+ + SO_3^{2-}$$

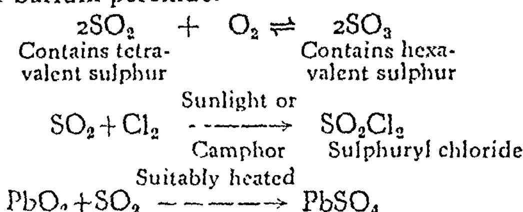
It is, therefore, called sulphurous anhydride. It turns blue litmus red, neutralizes alkalis and decomposes carbonates forming two well-known series of salts, *sulphites* and *bisulphites*. In addition to these metabisulphites, *e.g.*, potassium metabisulphite, $K_2S_2O_5$ are also salts of sulphurous acid though less common.



$$NaOH + SO_2 \rightarrow NaHSO_3$$
$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$
$$Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2$$

Sulphurous acid is known only in dilute solution. It loses whole of its sulphur dioxide on boiling.

(4) **Unsaturated Nature.** Sulphur is hexavalent but in sulphur dioxide (SO_2) only four valencies of sulphur are satisfied by two atoms of oxygen. The remaining two valencies of sulphur remain unsatisfied and render sulphur dioxide an unsaturated compound. It gives addition products with oxygen, chlorine and lead oxide or barium peroxide.



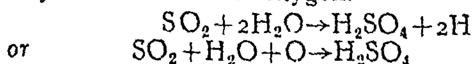
$$\underset{\text{Contains tetra-valent sulphur}}{2SO_2} + O_2 \rightleftharpoons \underset{\text{Contains hexa-valent sulphur}}{2SO_3}$$

$$SO_2 + Cl_2 \xrightarrow[\text{Camphor}]{\text{Sunlight or}} \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}$$

$$PbO_2 + SO_2 \xrightarrow{\text{Suitably heated}} PbSO_4$$

Expt. 1. Heat some lead dioxide in a deflagrating spoon and introduce in jar of sulphur dioxide. Lead dioxide becomes incandescent and changes into lead sulphate (*white*).

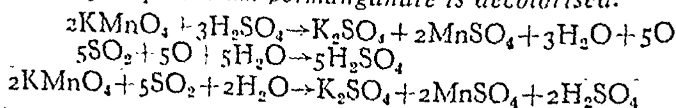
(5) **Reducing Property.** In presence of moisture it can liberate nascent hydrogen or in presence of an oxidizing agent it can easily take an atom of oxygen.



$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$
or
$$SO_2 + H_2O + O \rightarrow H_2SO_4$$

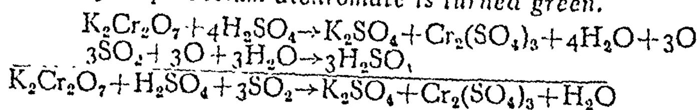
In both the above cases it acts as a strong reducing agent. Following are a few examples of its reducing properties :

(i) *Acidified potassium permanganate is decolorised.*



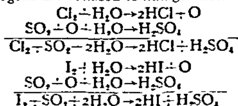
$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$5SO_2 + 5O + 5H_2O \rightarrow 5H_2SO_4$$
$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(ii) *Acidified potassium dichromate is turned green.*



$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
$$3SO_2 + 3O + 3H_2O \rightarrow 3H_2SO_4$$
$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

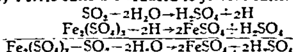
(iii) *Halogens are reduced to halogen acids.*



$$Cl_2 + H_2O \rightarrow 2HCl + O$$
$$SO_2 + O + H_2O \rightarrow H_2SO_4$$
$$\overline{Cl_2 + SO_2 + 2H_2O \rightarrow 2HCl + H_2SO_4}$$

$$I_2 + H_2O \rightarrow 2HI + O$$
$$SO_2 + O + H_2O \rightarrow H_2SO_4$$
$$\overline{I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4}$$

(iv) *Ferric salts are reduced to ferrous salts.*



$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H$$
$$Fe_2(SO_4)_3 + 2H \rightarrow 2FeSO_4 + H_2SO_4$$
$$\overline{Fe_2(SO_4)_3 + SO_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4}$$

(6) **Bleaching and Disinfecting Properties.** In the pre ence of moisture, sulphur dioxide reduces the vegetable colourin matter to colourless reduction product. It is, therefore, often use as a bleaching agent. On standing in air, the colourless reductio product is reoxidised by atmospheric oxygen to the original colou Bleaching with sulphur dioxide is, therefore, of a temporary natur

In certain cases sulphur dioxide forms a colourless additio product with vegetable colouring matter. Here the colour restored by treatment with sulphuric acid which decomposes th colourless addition product liberating sulphur dioxide. Thus th bleaching action of sulphur dioxide can be summarized as follows

Colourless reduction product	Reduced by SO_2 ← / → Re-oxidised by air	Vegetable colouring matter	Addition with SO_2 → / ← Decomposition by H_2SO_4	Colourle addition product

It is used for bleaching delicate articles, *e.g.*, straw silk, wool etc., which would be damaged by chlorine.

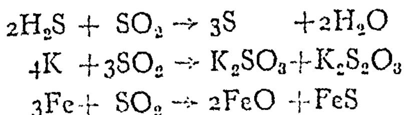
[illegible]

CHLORINE	SULPHUR DIOXIDE
(i) Bleaching is due to the oxidation of colouring matter to colourless oxidation product or due to the addition of Cl_2 to form colourless addition product.	(i) Bleaching is due to the redu tion of colouring matter colourless reduction produ or due to the formation colourless addition produ with SO_2
(ii) The bleaching is permanent and the colour is not restored on standing.	(ii) The bleaching is temporar and the colour is restored o standing in air or dipping i dilute acid.
(iii) Used for bleaching wood, paper pulp and cotton fabrics. But not for delicate articles.	(iii) Used for bleaching delica articles, e.g., straw, silk, wo etc. which would be damage by chlorine.

Sulphur dioxide is used as a disinfectant. This property is probably due to its activity and ability to exclude oxygen.

Expt. 2. Fill two jars with sulphur dioxide. Add red magenta dye to one, it is decolorised. Add a few moist flowers to the second jar and shake. The flowers turn white but regain their colour when dipped in dilute sulphuric acid.

(7) **Oxidising Property.** Its reaction with hydrogen sulphide, sodium, potassium, magnesium and iron shows that sulphur dioxide acts as an oxidising agent also.



$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

$$4K + 3SO_2 \rightarrow K_2SO_3 + K_2S_2O_3$$

$$3Fe + SO_2 \rightarrow 2FeO + FeS$$

Expt. 3. Bubble sulphur dioxide gas through a solution of hydrogen sulphide in water. Yellow precipitate of colloidal sulphur is obtained.

5. **Tests for Sulphur Dioxide.**—(*i*) It is a colourless gas with characteristic pungent smell of burning sulphur.

(*ii*) It turns potassium dichromate paper green.

6. **Uses.**—Several important uses of sulphur dioxide are:

(i) For the manufacture of sulphuric acid and sulphites, *e.g.*, calcium bisulphite is extensively used in the paper industry.

(*ii*) For bleaching delicate articles and for refining sugar.

(*iii*) As a disinfectant and household fumigation.

(*iv*) Liquid sulphur dioxide is used as an organic solvent.

(*v*) In household refrigerators sulphur dioxide is used as the refrigerant. It is condensed by compression and cooling. Cooling is caused when liquid sulphur dioxide is allowed to evaporate.

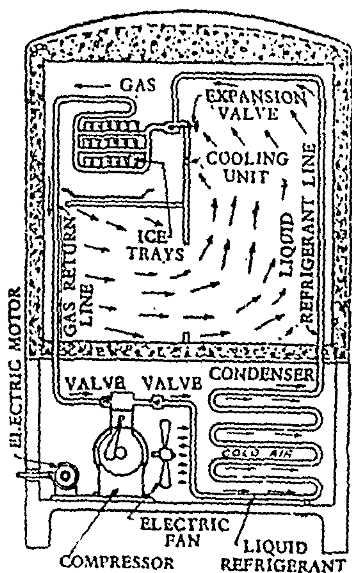
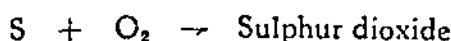


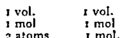
Fig. 37'2—A household refrigerator.

7. **Composition.**—(*a*) Volumetric. Volumetric composition of sulphur dioxide is determined in the type of apparatus shown in Fig. 37'3. A piece of sulphur is placed on the platinum loop *A* and some dry oxygen is enclosed in the bulb. The level of mercury is equalised in the two limbs and the volume of oxygen noted.

Electric current is passed through the platinum loop which gets heated and burns sulphur to sulphur dioxide. On cooling, no change in volume is noticed showing thereby that one volume of oxygen combines with sulphur to produce one volume of sulphur dioxide.



$$S + O_2 \rightarrow \text{Sulphur dioxide}$$



1 vol.	1 vol.
1 mol	1 mol
2 atoms	1 mol.

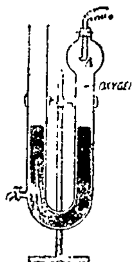


Fig. 37.3—Determination of the composition of sulphur dioxide.

Applying Avogadro's law to the above we conclude that one molecule of oxygen (=2 atoms) combines with sulphur (say, x atoms) to produce one molecule of sulphur dioxide, *i.e.*, formula of sulphur dioxide is S_xO_2 with molecular weight$=32x+32$.

Molecular weight of sulphur dioxide as calculated from its vapour density (=32) data is found to be$=2\times32=64$.

Equating this with the molecular weight as calculated from its formula S_xO_2, we get

$$32x+32=64 \quad \text{whence} \quad x=1$$

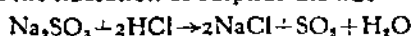
∴ Molecular formula of sulphur dioxide is SO_2.

(*b*) GRAVIMETRIC To determine gravimetric composition of sulphur dioxide, a known weight of sulphur is burnt in a current of pure dry oxygen. Sulphur dioxide produced is absorbed in weighed caustic potash bulbs. The increase in weight of potash bulbs gives the weight of sulphur dioxide obtained From this we calculate the weight of oxygen that combines with a fixed weight of sulphur. It is found that 32 parts by weight of oxygen combine with 32 parts by weight of sulphur.

8 **Sulphites and Bisulphites** Sulphurous acid is a dibasic acid and gives rise to two series of salts The normal salts (M_2SO_3) are called sulphites whereas the acid salts ($MHSO_3$) are known as bisulphites These are prepared by the action of sulphur dioxide on alkalis or carbonates Insoluble sulphites are obtained by double decomposition

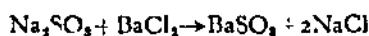
Their General Properties · (i) Alkali metal sulphites are soluble in water giving colourless, odourless solutions alkaline towards litmus due to hydrolysis. Bisulphite solutions are acidic and smell of sulphur dioxide

(ii) **Action of acids.** These are decomposed by dilute acids, hydrochloric or sulphuric acid with the liberation of sulphur dioxide



$$Na_2SO_3+2HCl\rightarrow2NaCl+SO_2+H_2O$$

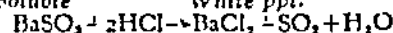
(iii) **Action of barium chloride** With barium chloride soluble sulphites give a white precipitate of barium sulphite which is soluble in hydrochloric acid.



$$Na_2SO_3+BaCl_2\rightarrow BaSO_3+2NaCl$$



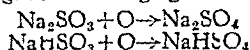
Soluble *White ppt.*



$$BaSO_3+2HCl\rightarrow BaCl_2+SO_2+H_2O$$

(*iv*) Action of silver nitrate. With silver nitrate an aqueous solution of a sulphite gives a white precipitate of silver sulphite soluble in dilute nitric acid.

(*v*) Reducing property. Like sulphurous acid sulphites and bisulphites can easily take up an atom of oxygen to give sulphates and bisulphates. These are, therefore, good reducing agents.



$$Na_2SO_3 + O \rightarrow Na_2SO_4$$
$$NaHSO_3 + O \rightarrow NaHSO_4$$

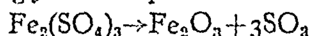
They reduce acidified potassium permanganate or dichromate solution. Halogens are reduced to hydracids and iodates to iodine by them (*see* page 2·80).

(*vi*) Sodium metabisulphite, $Na_2S_2O_5$ or $Na_2O.2SO_2$ is obtained by evaporating sodium bisulphite solution in excess of sulphur dioxide. This is used in photography.

SULPHUR TRIOXIDE, SO_3

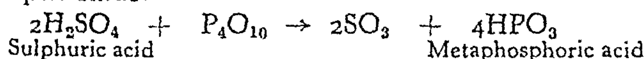
9. **Preparation of Sulphur Trioxide.**—Sulphur trioxide is obtained :

(*i*) *By heating ferric sulphate.*



$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

(*ii*). *By dehydration of sulphuric acid.* Sulphur trioxide is obtained when concentrated sulpuric acid is distilled with phosphorus pentoxide.



$$\underset{\text{Sulphuric acid}}{2H_2SO_4} + P_4O_{10} \rightarrow 2SO_3 + \underset{\text{Metaphosphoric acid}}{4HPO_3}$$

(*iii*) *Laboratory Method.* It is prepared in the laboratory by passing a mixture of dry sulphur dioxide and oxygen over platinised asbestos heated in a combustion tube as shown in the diagram (Fig. 37·4). Sulphur trioxide formed is collected in an ice-cooled receiver.

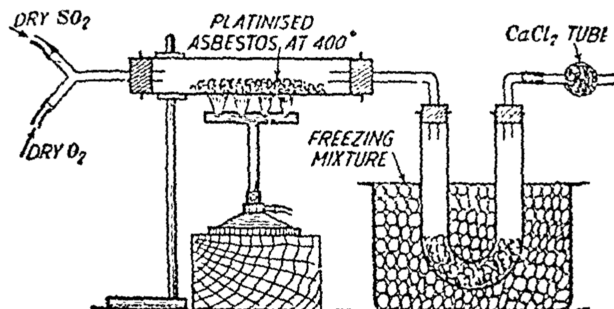
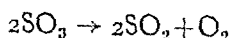


Fig. 37·4—Laboratory preparation of sulphur trioxide.

10. **Properties of Sulphur Trioxide.**—(*i*) Sulphur trioxide gives white transparent crystals which sublime on heating.

(*ii*) *Action of heat.* Sulphur trioxide when heated decomposes into sulphur dioxide and oxygen. Decomposition is complete at 1000°C.



$$2SO_3 \rightarrow 2SO_2 + O_2$$

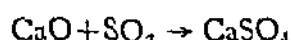
(*iii*) *Action of water.* It has a great affinity for water and dissolves in it with hissing sound giving a mist of fine droplets of sulphuric acid. It fumes strongly in moist air.

(*iv*) *Formation of oleum.* Sulphur trioxide dissolves in concentrated sulphuric acid to give oleum (fuming sulphuric acid or pyrosulphuric acid).



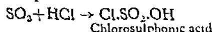
$$H_2SO_4+SO_3 \rightarrow H_2S_2O_7$$

(*v*) *Acidic nature.* It is an acidic oxide, the anhydride of sulphuric acid. With alkalis, carbonates or basic oxides, it gives sulphates.



$$CaO+SO_3 \rightarrow CaSO_4$$

(*vi*) *With hydrochloric acid*, sulphur trioxide gives an addition product, chlorosulphonic acid.



$$SO_3+HCl \rightarrow Cl.SO_2.OH$$

Chlorosulphonic acid

11. Uses.—Sulphur trioxide is used :

(i) In the manufacture of sulphuric acid and oleum.

(ii) For drying gases.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between

1. Burning of sulphur in air or roasting of zinc sulphide

2. Hot conc. sulphuric acid+(i) Sulphur, (ii) Carbon, (iii) Copper, (iv) Phosphorus pentoxide.

3. Dilute sulphuric acid+(i) Sodium sulphite, (ii) Sodium bisulphite.

4. Burning of (i) Magnesium, (ii) Sodium in sulphur dioxide

5. Sulphur dioxide+(i) When strongly heated, (ii) Sodium hydroxide, (iii) Oxygen, (iv) Chlorine, (v) Lead dioxide, (vi) Acidified potassium permanganate, (vii) Acidified potassium dichromate, (viii) Chlorine, (ix) Iodine, (x) Ferric sulphate, (xi) Hydrogen sulphide, (xii) Iron

6. Ferric sulphate heated strongly

7. Sulphur trioxide+(i) Heated, (ii) Water (iii) Sulphuric acid, (iv) Calcium oxide, (v) Hydrochloric acid.

QUESTIONS

Essay-type Questions

1. How is sulphur dioxide prepared [illegible] ? Give examples of the reactions in which sulphur dioxide [illegible] as a reducing agent, (*b*) as an oxidising agent and (*c*) as an [illegible]

2. Describe with the help of a diagram [illegible] collection of a sample of sulphur dioxide [illegible] formula ? What is the action of gas on [illegible] hydrogen, (c) Acidified dichromate solution ?

3. How is sulphur dioxide [illegible] uses ? How does it react with [illegible] ferric chloride ? Compare the [illegible] chlorine. [illegible]

4. Name two important [illegible] can these be prepared from [illegible] ?

Which of these is an [illegible] giving one example for each [illegible]

5. Describe the laboratory method for the preparation of sulphur dioxide. Give two reactions in each case to show that it is oxidising and reducing in character and give one reaction to establish its acidic nature.

(Punjab Pre-Univ. 1962)

6. How is sulphur dioxide prepared in the laboratory ? Give its important properties and uses. How is it tested ? How would you determine its gravimetric composition ?

7. Give the preparation of sulphur trioxide from sulphur and its uses.

Test Your Understanding

8. Strike off the word/words not required :

(i) Only dry/moist sulphur dioxide will act as bleaching agent.

(ii) Decolorisation of potassium permanganate solution is the reducing/oxidising property of sulphur dioxide.

(iii) Bleaching with sulphur dioxide is temporary/permanent.

(iv) Sulphur dioxide reduces/oxidises hydrogen sulphide.

9. Fill in the blanks :

(a) When iron pyrites are burnt in air......and......are formed.

(b) Bleaching action of SO_2 is due to its......property.

(c) Metals like......and..... burn in SO_2 as......

(d) When Cl_2 is passed through SO_2 solution......formed.

(e) When ferric sulphate is heated......obtained.

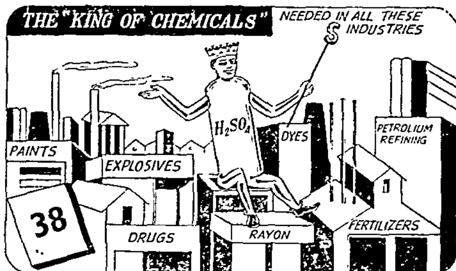
(f) Oleum can be obtained by dissolving......in......

(g) HCl and SO_3 produce......

KEY

8. (i) moist ; (ii) reducing ; (iii) temporary ; (iv) oxidises.

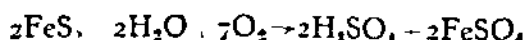
9. (a) Fe_2O_3, SO_2 ; (b) Reducing ; (c) K ; Mg ; they are highly ele positive ; (d) H_2SO_4 and HCl are ; (e) Fe_2O_3, SO_2 and SO_3 ; (f) SO_3 ; C H_2SO_4 ; (g) Chlorosulphonic acid.



Acids of Sulphur

SULPHURIC ACID, H_2SO_4

1. **Historical and Occurrence**.—Earliest mention of sulphuric acid is probably seen in the writings of Geber (ninth century) in Latin. In the later middle ages it was called *oil of vitriols* and was prepared by distilling ferrous sulphate crystals (green vitriol). Free acid is found in certain mineral springs and is formed there by the action of water on sulphides, *e.g.*, iron pyrites.

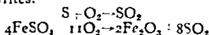


$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2H_2SO_4 + 2FeSO_4$$

2. **Manufacture of Sulphuric Acid**.—Sulphuric acid at present is the most important sulphur compound in industry and the manufacture of sulphuric acid is one of the most important world industries. It is manufactured either by the *Lead Chamber Process* or by the *Contact Process*.

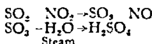
3. **The Lead Chamber Process**.—The lead chamber process for the manufacture of sulphuric acid dates back to about 200 years. Although less efficient than the contact process, it is still of considerable commercial importance.

Theory. (i) Sulphur dioxide is obtained by burning sulphur or roasting pyrites.



$$S + O_2 \rightarrow SO_2$$
$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(ii) Sulphur dioxide obtained above is oxidised by oxides of nitrogen to sulphur trioxide which reacts with steam to produce sulphuric acid.



$$SO_2 + NO_2 \rightarrow SO_3 + NO$$
$$SO_3 + \underset{\text{Steam}}{H_2O} \rightarrow H_2SO_4$$

Nitric oxide produced takes oxygen from air and gets converted back to nitrogen dioxide. Thus oxides of nitrogen take oxygen from air and pass it on to sulphur dioxide and thus act as *oxygen carriers.*

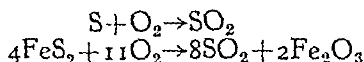


$$2NO + O_2 \rightarrow 2NO_2$$

It is seen that in the presence of an insufficient quantity of steam or water spray, lead chamber crystals of the composition $HSO_4.NO$ (*nitroso-sulphuric acid*) are obtained. This, however, does not prove that nitroso-sulphuric acid is an intermediate product in the manufacture of sulphuric acid under normal conditions.

Plant used. The plant used (*Fig.* 38·1) consists of the following parts :

(*i*) **Pyrites or sulphur burners.** These are specially designed brick furnaces where sulphur or iron pyrites are burnt to produce sulphur dioxide. They are provided with a special arrangement to turn them over to drop the residue into the ash pit.



$$S + O_2 \rightarrow SO_2$$
$$4FeS_2 + 11O_2 \rightarrow 8SO_2 + 2Fe_2O_3$$

Sulphur dioxide mixed with air from the burners is purified to remove traces of arsenic and dust and then passed on to the Glover tower.

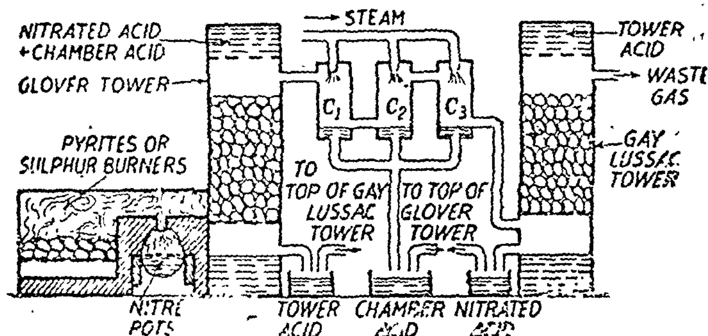
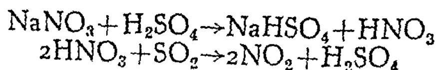


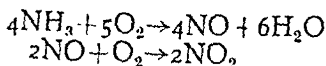
Fig. 38·1—Lead Chamber Process sulphuric acid plant.

(*ii*) **Nitre pots.** Here nitre is heated with concentrated sulphuric acid to produce nitric acid which mixes with sulphur dioxide on its way to Glover tower and is reduced to nitrogen dioxide in the transit.



$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
$$2HNO_3 + SO_2 \rightarrow 2NO_2 + H_2SO_4$$

The modern practice for getting oxides of nitrogen is by catalytic oxidation of ammonia. A mixture of ammonia (1 vol.) with air (8 vols.) is passed over a catalyst (platinum gauze at 800°C).



$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$

(iii) **Glover Tower.** It is a steel tower lined inside with sheet lead or acid-resisting bricks. It is packed with flint stone, quartz or some acid resisting bricks. The hot gases (sulphur dioxide+air+oxides of nitrogen) pass up this tower while dilute chamber acid and nitrated acid (from the Gay-Lussac tower) are flowing down slowly over flint stone.

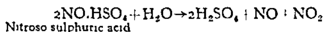
Flint stone serves to retard the upward flow of gases and thus expose them for a longer time to the sulphuric acid which trickles down. Here again we come across an example of the application of the *principle of counter-currents.*

Various functions of this tower are :

(*a*) The hot gases rising up are cooled down from 300—400°C to about 70°C.

(*b*) Dilute chamber acid trickling down is concentrated to about 80 per cent.

(*c*) The nitrated acid from the Gay-Lussac tower flowing down the Glover tower is denitrated.



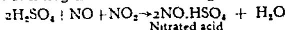
$$\underset{\text{Nitroso sulphuric acid}}{2NO.HSO_4} + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$$

(*d*) Some sulphur dioxide is actually converted to sulphuric acid (*see* theory above).

The tower acid is drawn off from the bottom of the tower and collected into a container called *acid egg*.

(*iv*) **Lead Chambers.** These are big chambers about 12×6×30 meters, generally two to four in number (C_1, C_2, C_3), rectangular or cylindrical in shape and made of sheet lead supported in wooden frames. Lead is selected for the purpose as it is least affected by the chamber acid Very fine spray of water or steam is blown into these chambers from near the top. Their *main function* is to afford a prolonged contact between interacting gases which combine (as explained in theory) to produce sulphuric acid. Reactions not completed in the first lead chamber are continued in the second and third chambers Dilute sulphuric acid obtained in any of these chambers is called Chamber acid. It flows down into a common receiver and is about 65 per cent. A part of the chamber acid is pumped up to the top of Glover tower while the rest is sent for concentration.

(*v*) **Gay-Lussac Tower** The residual gases (mainly air+oxides of nitrogen) from the lead chambers are passed up another tower called Gay-Lussac tower, lined with sheet lead and packed with coke. A stream of cold concentrated sulphuric acid pumped from the base of Glover tower is allowed to trickle down when it absorbs oxides of nitrogen from the residual gases.



$$2H_2SO_4 + NO + NO_2 \rightarrow \underset{\text{Nitrated acid}}{2NO.HSO_4} + H_2O$$

The nitrated acid flows down and is pumped on to the top of the Glover tower.

(*vi*) **Chimney.** A chimney placed on the extreme right of the plant (not shown in the diagram) maintains the necessary draught to keep the gases circulating through the system.

A chamber process sulphuric acid plant is not spread out in the manner shown in Fig. 38·1. It is given there only for the sake of explanation. A floor plan of the plant is given in Fig. 38·2 to show how compact the plant is in practice.

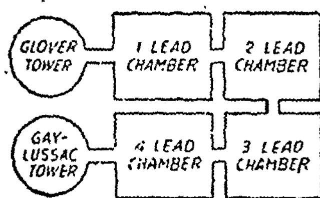
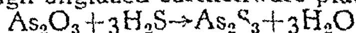


Fig. 38·2—Floor plan of the Chamber Process plant.

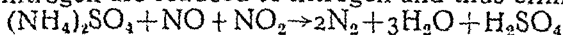
4. **Principal Impurities present in the Chamber Acid and their removal.**—The chief impurities present in the chamber acid are arsenious oxide (from pyrites), lead sulphate (from the action of sulphuric acid on lead chambers) and oxides of nitrogen. These are removed as follows :

The acid is diluted with water when lead sulphate is precipitated. On passing hydrogen sulphide through the diluted acid, arsenious oxide is precipitated as arsenious sulphide. This is filtered off through unglazed earthenware plates by suction.



$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

The filtered acid is distilled over ammonium sulphate when oxides of nitrogen are reduced to nitrogen and thus eliminated.



$$(NH_4)_2SO_4 + NO + NO_2 \rightarrow 2N_2 + 3H_2O + H_2SO_4$$

It is not always necessary to purify chamber acid. For most purposes it is used as such. Pure acid, whenever needed, is prepared by the contact process rather than by purification of the chamber acid.

5. **Concentration of the Chamber Acid.**—Sulphuric acid obtained from the chambers is always dilute. A part of it is poured at the top of the Glover tower where it is concentrated by the hot gases rising up. The tower acid collected at the bottom of the Glover tower is about 80 per cent. A great deal of the remaining chamber acid is concentrated further in a number of ways. Two of them may be mentioned here.

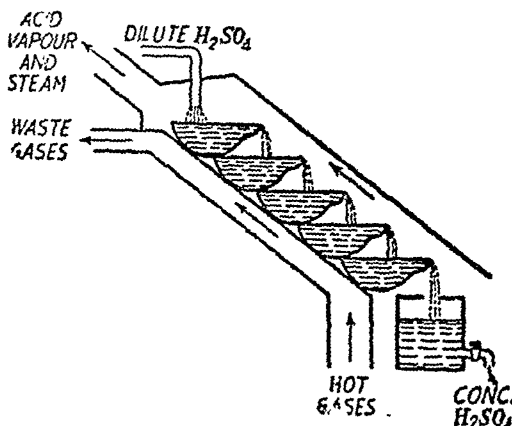


Fig. 38·3—The Cascade Process.

(*a*) **The Cascade Process.** Here a number of silica dishes are arranged one above the other on stairs

made of acid-proof bricks. They are heated by hot gases rising from a furnace below. Dilute acid

gets concentrated as it moves from one dish to the next and thus passes through zones of higher and higher temperature. By the time it collects below, it is about 93—95 per cent sulphuric acid.

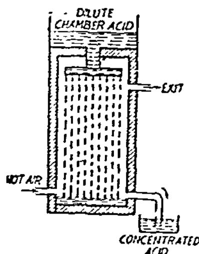
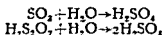


Fig. 35 4—The Gaillard tower.

(*b*) **The Gaillard Tower.** A cheaper and perhaps the most successful method, particularly when large quantities of acid have to be dealt with, is concentration by means of the Gaillard tower. The tower is built of the acid-resisting stones or bricks. Dilute acid falls down in the form of very fine spray

oncentration of the The concentrated 5 per cent sulphuric acid.

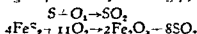
Last traces of water are removed, if needed, by adding sulphur trioxide or oleum.



$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

6. **The Contact Process for the manufacture of Sulphuric Acid.**—Whereas the Lead Chamber Process involves the relatively easier oxidation of sulphur dioxide with the help of oxides of nitrogen in presence of water, the Contact Process attempts, as given below, the much more difficult direct oxidation of dry sulphur dioxide to sulphur trioxide.

(*a*) **Theory of the Contact Process.** (*i*) Sulphur dioxide is produced by burning sulphur or by roasting pyrites.



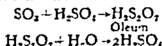
$$S + O_2 \rightarrow SO_2$$
$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

(*ii*) Sulphur dioxide obtained is oxidised catalytically to sulphur trioxide with atmospheric oxygen.



$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

(*iii*) Sulphur trioxide produced is absorbed in sulphuric acid to get oleum which is further diluted with water to get sulphuric acid of desired concentration.

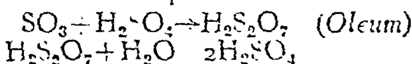


$$SO_3 + H_2SO_4 \rightarrow \underset{\text{Oleum}}{H_2S_2O_7}$$
$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

pass down through the catalyst. As a result of oxidation of sulphur dioxide to sulphur trioxide heat produced once again raises the temperature of catalyst which is again cooled to 450°C· by upgoing gases.

In the Grillo process the catalyst is arranged on shelves provided in the converter.

(4) **Absorption Tower.** Sulphur trioxide from the contact tower is passed up the absorption tower where it meets a descending stream of concentrated sulphuric acid. Sulphur trioxide is absorbed by sulphuric acid when *oleum* is obtained. This can be diluted to obtain any desired concentration of the acid. With water sulphur trioxide gives a dense fog of sulphuric acid particles, hence water is not used for absorption.



$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7 \quad (\textit{Oleum})$$
$$H_2S_2O_7 + H_2O \quad 2H_2SO_4$$

Sulphuric Acid Industry in India

	Installed Capacity (in thousand tonnes)	Production (in thousand tonnes)
1960-61	550	360
1965-66	1,500	1.200
1970-71	3,500	3.000
1975-76	6,000	6.000

7. Laboratory Demonstration of the Contact Process.—Manufacture of sulphuric acid can be demonstrated in the laboratory as shown in Fig. 38·7. Sulphur burning in a small crucible produces sulphur dioxide which is passed through the catalyst heated in a pyrex tube. Here sulphur dioxide is oxidised to sulphur trioxide which bubbles through water to produce sulphuric acid. Water pump on the right acts as a suction pump and keeps the gases circulating through the system.

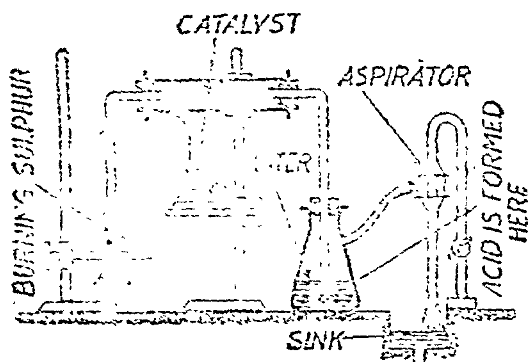


Fig. 38·7—Laboratory demonstration of the Contact Process.

Note. Those who have been to D.C.M. Chemical Works, Delhi, or some other similar works might have noticed that the purification unit was conspicuous by its absence. What they do there is that pure American sulphur is melted in a tank. The molten sulphur is taken into another tank and air is blown through it. Sulphur burns to give sulphur dioxide which is quite pure. This is passed through a big iron tower having three layers of the catalyst packing at different heights. The gases pass through the lower packing, get heated and partially converted to sulphur trioxide. The resulting mixture is cooled and passed through the middle packing and similarly through the upper packing. Sulphur trioxide passing out at the top is cooled and absorbed in sulphuric acid to get oleum which is diluted to obtain sulphuric acid.

8. Comparison between the two Processes used for the manufacture of Sulphuric Acid.—(*i*) Sulphuric acid obtained by the chamber process is dilute and impure whereas one obtained by the contact process is extremely pure and concentrated. In fact acid of any concentration can be obtained by the contact process.

(*ii*) There was a time when the chamber process was considered to be cheaper and easier to control. Contact process was expensive due to its platinized asbestos which was costly and got poisoned very soon. It needed an elaborate control due to its purification unit.

With the use of American sulphur for getting sulphur dioxide and cheaper vanadium pentoxide (immune to the action of poisons), the contact process is quite cheap and is easier to control.

(*iii*) Chamber process is still being used for the manufacture of sulphuric acid used for a number of purposes *e.g.*, for the manufacture of superphosphate of lime, we do not require pure and concentrated acid. Of course, new plants set up are mostly the contact process plants while the old chamber acid plants are being slowly replaced by contact plants.

9. Properties of Sulphuric acid.

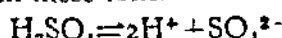
(*a*) **Physical.** (i) It is a colourless syrupy liquid (Sp. Gr. 1·84 at 15°C).

(*ii*) It boils at 338°C when it is found to contain only 98·3 per cent of the acid. Thus concentration beyond 98·3 per cent cannot be effected by boiling. Pure 100 per cent acid is obtained by dissolving sulphur trioxide in dilute acid.

(*iii*) Concentrated acid fumes strongly in moist air.

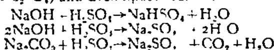
(*b*) **Chemical.** Its chemical reactions can be studied under the following heads :

(1) **Ionic Reactions.** Sulphuric acid ionizes in solution to give hydrogen ions and sulphate ions. Thus in solution, it exhibits the reactions of both these ions.



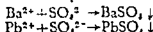
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

(*i*) *Those of hydrogen ions.* Sulphuric acid is a typical dibasic acid. Due to the hydrogen ions which it gives in solution, it possesses all the common properties of an acid, *e.g.*, sour taste, turns blue litmus red, neutralizes alkalis to give series of salts ($NaHSO_4$ and Na_2SO_4) and decomposes carbonates.



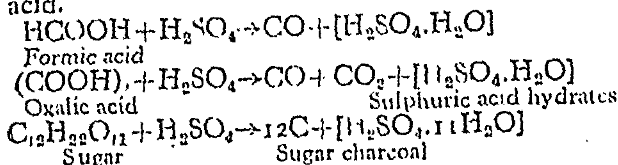
$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$$
$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$
$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + H_2O$$

(*ii*) *Those of sulphate ions.* It gives white precipitate of barium sulphate and lead sulphate with all barium and lead salts.



$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$$
$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4 \downarrow$$

(2) **Affinity for water.** It dissolves in water with evolution of heat, forms hydrates with water and is, therefore, used as a dehydrating agent. Its *corrosive action on skin is due to dehydration* of skin which then burns and produces the itching sensation. Charring of wood, paper, sugar and preparation of carbon monoxide from the oxalic or formic acid are all *dehydrating properties* of sulphuric acid.

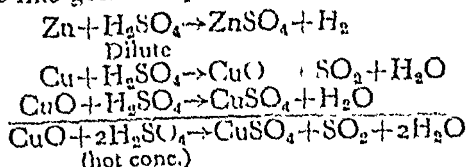


$$\underset{\text{Formic acid}}{HCOOH} + H_2SO_4 \rightarrow CO + [H_2SO_4.H_2O]$$

$$\underset{\text{Oxalic acid}}{(COOH)_2} + H_2SO_4 \rightarrow CO + CO_2 + \underset{\text{Sulphuric acid hydrates}}{[H_2SO_4.H_2O]}$$

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} + H_2SO_4 \rightarrow \underset{\text{Sugar charcoal}}{12C} + [H_2SO_4.11H_2O]$$

(3) **Action on metals.** (*i*) Metals like iron, zinc, aluminium, tin and manganese react with dilute acid to liberate hydrogen; (*ii*) metals like lead, copper, mercury and silver react with hot concentrated sulphuric acid to produce sulphur dioxide while (*iii*) noble metals like gold and platinum do not react at all.



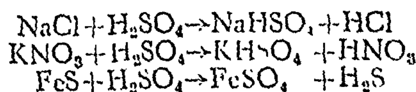
$$Zn + \underset{\text{Dilute}}{H_2SO_4} \rightarrow ZnSO_4 + H_2$$

$$Cu + H_2SO_4 \rightarrow CuO + SO_2 + H_2O$$

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

$$CuO + \underset{\text{(hot conc.)}}{2H_2SO_4} \rightarrow CuSO_4 + SO_2 + 2H_2O$$

(4) **Action on salts.** It is a strong acid and decomposes the salts of the more volatile acids, *e.g.*, chlorides, nitrates, sulphites, carbonates, sulphides, etc. Corresponding acid is liberated in each case.



$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$$

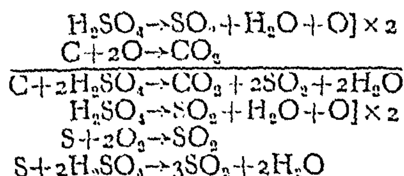
$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

(5) **Oxidising action.** Due to the fact that it can easily supply an atom of oxygen, it acts as an active oxidizing agent.



$$H_2SO_4 \rightarrow SO_2 + H_2O + O$$

(*i*) It oxidises carbon and sulphur to their corresponding oxides.



$$H_2SO_4 \rightarrow SO_2 + H_2O + O] \times 2$$

$$C + 2O \rightarrow CO_2$$

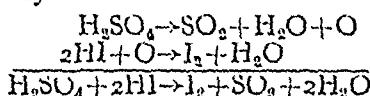
$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$

$$H_2SO_4 \rightarrow SO_2 + H_2O + O] \times 2$$

$$S + 2O_2 \rightarrow SO_2$$

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

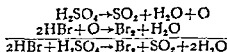
(*ii*) Hydrobromic and hydriodic acids are oxidised to bromine and iodine respectively.



$$H_2SO_4 \rightarrow SO_2 + H_2O + O$$

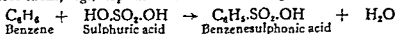
$$2HI + O \rightarrow I_2 + H_2O$$

$$H_2SO_4 + 2HI \rightarrow I_2 + SO_2 + 2H_2O$$



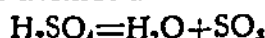
$$H_2SO_4 \rightarrow SO_2 + H_2O + O$$
$$2HBr + O \rightarrow Br_2 + H_2O$$
$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

(6) **With aromatic compounds.** Sulphuric acid reacts with aromatic organic compounds and gives either sulphonic acids or oxidises them, *e.g.*, naphthalene is oxidised to phthalic acid.



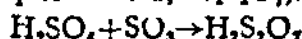
$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Sulphuric acid}}{HO.SO_2.OH} \rightarrow \underset{\text{Benzenesulphonic acid}}{C_6H_5.SO_2.OH} + H_2O$$

(7) **Dissociation.** On boiling sulphuric acid free from water, it dissociates into sulphur trioxide and water.



$$H_2SO_4 = H_2O + SO_3$$

(8) **With sulphur trioxide.** It dissolves sulphur trioxide to give oleum (pyrosulphuric acid, $H_2S_2O_7$).



$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

10. **Uses [illegible]**
Sulphuric acid i[illegible]
ant is this acic [illegible]
the "King of Chemicals". The yearly consumption of sulphuric acid is an index to industrialization, prosperity or civilization of a country. The chief uses of the acid are :

(1) *In fertilizer industry.* It is used in the manufacture of ammonium sulphate and superphosphate of lime.

(2) *In refining petroleum.* Crude petroleum is agitated with sulphuric acid to remove objectionable sulphur and tarry compounds.

(3) *In chemical industries.* Sulphuric acid is employed in the manufacture of other acids (hydrochloric, nitric and phosphoric acids), sulphates and ether.

(4) *In dyes and drugs.* The acid is used in the manufacture of coal-tar dyes and drugs. It is used there for sulphonation and dehydration purposes.

(5) *For pickling.* It is used for cleansing metals (removing the oxide layer from their surface) before enamelling, electroplating, galvanizing or soldering.

(6) *In the manufacture of explosives.* Dynamite, T.N.T and picric acid are obtained by the action of sulphuric and nitric acids mixture on organic compounds.

(7) *In metallurgy.* A number of metals, *e g*, copper, are extracted from their ores using sulphuric acid.

(8) *In storage batteries.*

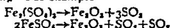
(9) *In the manufacture of nitrocellulose products.* It is used in the manufacture of textiles (cotton, wool and linen fabrics), rayon, photographic films, rubber and lacquers.

(10) *In the laboratory.* It is an important laboratory reagent, also used as a dehydrating and drying agent.

11. Sulphates and Bisulphates —Sulphuric acid is a dibasic acid and

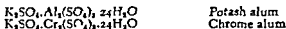
General Properties. (*i*) *Solubility* These are mostly stable and soluble in water. Exceptions are sulphates of alkaline earth metals and lead which are soluble.

(*ii*) *Action of heat* They are generally stable towards heat but some of them decompose on heating. For example



$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$
$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$$

(*iii*) *Formation of double salts* Soluble sulphates give double salts. For example, alkali metal sulphates (*e.g*, those of Na, K and NH_4^+) give alums with sulphates of trivalent metals, *e.g.*, those of Fe^{3+}, Cr^{3+} and Al^{3+}). Important alums are :



$K_2SO_4.Al_2(SO_4)_3.24H_2O$ Potash alum
$K_2SO_4.Cr_2(SO_4)_3.24H_2O$ Chrome alum

Similarly $FeSO_4(NH_4)_2SO_4.6H_2O$ is ferrous ammonium sulphate (Mohr's salt).

(*iv*) *Precipitation reactions.* Soluble sulphates give the reactions of sulphate ions (*see* page 2 147)

(*v*) *Reduction.* On fusing a mixture of a sulphate with charcoal powder, the sulphate is reduced to a sulphide.



$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

(*vi*) *Vitriols.* A number of sulphates crystallize out with a definite number of molecules of water of crystallization and are called *vitriols.* For example,



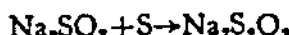
$CuSO_4.5H_2O$ *Blue vitriol*
$FeSO_4.7H_2O$ Green vitriol
$ZnSO_4.7H_2O$ White vitriol

THIOSULPHURIC ACID, $H_2S_2O_3$

n sodium thiosulphate is unstable and at once

13. Sodium Thiosulphate.—Most important salt of thiosulphuric acid is sodium thiosulphate, $Na_2S_2O_3.5H_2O$. Unlike thiosulphuric acid it is quite stable.

boiling ring till



$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

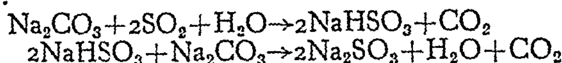
To the Students—To recall uses of sulphuric acid, remember

B C D E F — L M N — P P

These stand for—Batteries ; Chemical industries ; Dyes and Drugs ; Explosives ; Fertilizers—Laboratory reagent ; Metallurgy ; Nitrocellulose—Petroleum ; Pickling.

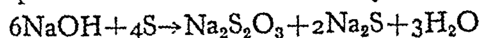
The excess of sulphur is filtered off and the filtrate evaporated to crystallization when crystals of sodium thiosulphate, $Na_2S_2O_3.5H_2O$ separate on slow cooling.

Sodium sulphite solution used above is prepared from sodium carbonate. A concentrated solution of sodium carbonate is prepared. One half of this is saturated with sulphur dioxide and the other half of the solution is then added when we get sodium sulphite.



$$Na_2CO_3+2SO_2+H_2O \rightarrow 2NaHSO_3+CO_2$$
$$2NaHSO_3+Na_2CO_3 \rightarrow 2Na_2SO_3+H_2O+CO_2$$

(*iii*) Sodium thiosulphate is also formed together with sodium sulphide when sulphur is boiled with sodium hydroxide solution.

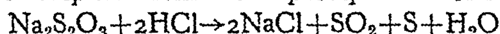


$$6NaOH+4S \rightarrow Na_2S_2O_3+2Na_2S+3H_2O$$

Properties. (*i*) *State.* It is a colourless, crystalline and efflorescent substance of the formula $Na_2S_2O_3.5H_2O$. It is soluble in water.

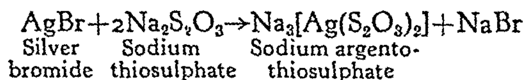
(*ii*) *Action of heat.* On heating it decomposes to give sulphur dioxide, hydrogen sulphide and sulphur.

(*iii*) *Action of dilute acids.* Dilute acids decompose it with the evolution of sulphur dioxide and precipitation of sulphur.



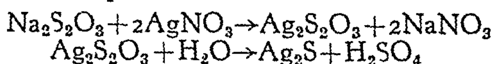
$$Na_2S_2O_3+2HCl \rightarrow 2NaCl+SO_2+S+H_2O$$

(*iv*) *Action of silver halides.* Silver halides are dissolved by sodium thiosulphate solution (*Hence used in photography for fixing*).



$$\underset{\text{Silver bromide}}{AgBr}+\underset{\text{Sodium thiosulphate}}{2Na_2S_2O_3} \rightarrow \underset{\text{Sodium argento-thiosulphate}}{Na_3[Ag(S_2O_3)_2]}+NaBr$$

(*v*) *Action of silver nitrate solution.* Silver nitrate gives, with a very dilute solution of it, a white precipitate which quickly changes colour to yellow, brown and finally black due to the formation of silver sulphide.



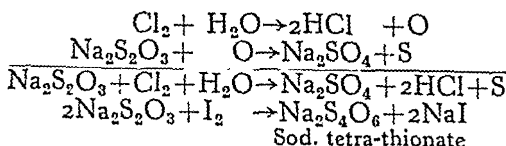
$$Na_2S_2O_3+2AgNO_3 \rightarrow Ag_2S_2O_3+2NaNO_3$$
$$Ag_2S_2O_3+H_2O \rightarrow Ag_2S+H_2SO_4$$

With a concentrated solution of sodium thiosulphate, silver nitrate gives no precipitate. This is because silver thiosulphate formed is readily soluble in excess of sodium thiosulphate.



$$Ag_2S_2O_3+3Na_2S_2O_3 \rightarrow 2Na_3[Ag(S_2O_3)_2]$$

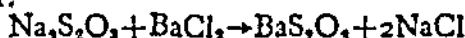
(*vi*) *Action with halogens.* *Chlorine* oxidises it to sodium sulphate while *Iodine* is decolorized due to the formation of tetrathionate.



$$Cl_2+H_2O \rightarrow 2HCl+O$$
$$Na_2S_2O_3+O \rightarrow Na_2SO_4+S$$
$$\overline{Na_2S_2O_3+Cl_2+H_2O \rightarrow Na_2SO_4+2HCl+S}$$
$$2Na_2S_2O_3+I_2 \rightarrow \underset{\text{Sod. tetra-thionate}}{Na_2S_4O_6}+2NaI$$

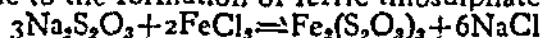
(*vii*) *With barium chloride solution.* A moderately concentrated solution of sodium thiosulphate gives a white precipitate of barium thiosulphate with barium chloride. No precipitate is

obtained with calcium chloride since calcium thiosulphate is fairly soluble in water.



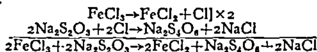
$$Na_2S_2O_3+BaCl_2 \rightarrow BaS_2O_3+2NaCl$$

(viii) With ferric chloride solution. On addition of a few drops of ferric chloride to thiosulphate solution, a violet coloration is obtained due to the formation of ferric thiosulphate (*violet*).



$$3Na_2S_2O_3+2FeCl_3 \rightleftharpoons Fe_2(S_2O_3)_3+6NaCl$$

The violet colour disappears quickly due to the reduction of ferric chloride by thiosulphate. This shifts the above equilibrium to the left.



$$[FeCl_3 \rightarrow FeCl_2+Cl] \times 2$$
$$2Na_2S_2O_3+2Cl \rightarrow Na_2S_4O_6+2NaCl$$
$$\overline{2FeCl_3+2Na_2S_2O_3 \rightarrow 2FeCl_2+Na_2S_4O_6+2NaCl}$$

Uses. Sodium thiosulphate is used :

(i) In photography. Due to its property of dissolving silver halides, it is used in photography for fixing under the name hypo.

(ii) In textile industry. During bleaching sodium thiosulphate is used as an antichlor.

(iii) In metallurgy. It is used in the extraction of gold and silver from their ores.

(iv) In the laboratory. It is used for the volumetric estimation of iodine and as a reagent.

(v) In medicine. Sodium thiosulphate is also used in medicine.

14. **Tests for Thiosulphates.**—Following properties of thiosulphates are used as analytical tests for them in the laboratory :

(i) *Action of heat.* A thiosulphate on heating gives out sulphur dioxide, hydrogen sulphide and sulphur.

(ii) *Action of dilute acids.* It gives out sulphur dioxide and a colloidal sulphur precipitate when treated with dilute acid.

(iii) *Action of silver nitrate.* A dilute solution of thiosulphate gives a white precipitate changing colour to yellow, brown and finally black when concentrated solution of a thiosulphate gives a white precipitate.

(iv) *Action of barium chloride.* With barium chloride, a concentrated solution of a thiosulphate gives a white precipitate.

(v) *Action of iodine solution.* Iodine solution is decolorised by a thiosulphate solution.

(vi) *Action with ferric chloride.* On adding a few drops of ferric chloride to thiosulphate, a violet colour is obtained which disappears quickly.

TEST YOURSELF ON THESE REACTIONS

Write equations, if any, between :

1. Sulphuric acid+Oxides of nitrogen+Ammonium sulphate
2. Nitrososulphuric acid+Water (*Heated*)
3. Sulphuric acid+(i) Caustic soda, (ii) Barium [illegible], (iii) Formic acid, (iv) Oxalic acid, (v) Sugar, (vi) Copper, [illegible] chloride, (viii) Potassium nitrate, (ix) Carbon or Sulphur, (x) [illegible] and, (xi) Benzene, (xii) Sulphur trioxide.
4. Action of heat on (i) Ferrous sulphate [illegible]
5. Sodium thiosulphate+(i) Hydrochloric acid, [illegible], (iii) Silver nitrate, (iv) Chlorine, (v) Iodine, (vi) [illegible], (vii) [illegible] chloride.

Distinguishing Tests for Sulphides, Sulphites, Thiosulphates and Sulphates.

Test	Sulphide	Sulphite	Thiosulphate	Sulphate
1. Treat the salt with cold dil. HCl.	H_2S is given off (Lead acetate paper blackened).	SO_2 is given off (turns dichromate paper green).	SO_2 evolved and sulphur precipitated.	No action. (Even with hot conc. H_2SO_4 there is no action.)
2. Add $BaCl_2$ to salt solution.	No ppt.	White ppt. of $BaSO_3$, soluble in HCl giving SO_2.	White ppt. of BaS_2O_3 with a concentrated solution of thiosulphate.	White ppt. of $BaSO_4$ insoluble in HNO_3.
3. Add $AgNO_3$ solution to the original salt solution.	Black ppt. of Ag_2S	White ppt. soluble in HNO_3.	White ppt. of $Ag_2S_2O_3$, changing colour to yellow, brown and finally black.	No action.
4. To the salt solution add $FeCl_3$ solution.	Black ppt.	Dark red coloration.	Purple coloration which disappears at once.	No action.
5. Confirmatory test.	(i) Add sodium nitroprusside solution. A violet colour obtained. (ii) Black ppt. obtained with lead acetate solution.	Iodine or $KMnO_4$ solution decolorised.	Iodine or $KMnO_4$ solution decolorised.	White ppt. obtained with lead acetate which is insoluble in ammonium acetate.

QUESTIONS

Essay-type Questions

1. Describe the Chamber Process of manufacturing sulphuric acid. What are the impurities present in the commercial acid and how are they removed? What is oleum and how can it be obtained?

Comment briefly on the statement that the amount of sulphuric acid manufactured in a country is an indication of the state of development of the chemical industry. *(U.P. Board Inter. 1963)*

2. (*a*) Describe the Contact Process for the manufacture of sulphuric acid. What are the important uses of the acid? What is the action of sulphuric acid on copper, potassium iodide, barium peroxide, oxalic acid, phosphorus, potassium chloride, cane sugar, formic acid and carbon?
(Punjab Pre-Univ. 1970 ; Delhi H.S. 1970 ; All-India H.S. 1971)

(*b*) How can sulphur dioxide be converted into sulphuric acid? Give the essential outlines of the process. *(Punjab Pre-Univ. 1971)*

3. How is sulphuric acid manufactured by the Contact Process? Why is this process superior to the Chamber Process?

It is said "Sulphuric acid is the backbone of many industries." Name some industries where sulphuric acid is needed.
(Punjab Inter. 1961 ; Kashmir 1961 ; Delhi H.S. 1968, 60 ; Punjab H.S. 1961, Delhi Pre Medical 1960 ; Delhi Pre-Univ. 1961)

4. [illegible] ...micals"? Describe [illegible] Sulphuric acid is [illegible] agent. Describe an [illegible]
(Punjab H.S. 1963, 62)

5. What functions do the oxides of nitrogen play in the Lead Chamber Process for the manufacture of sulphuric acid?

Why has the Contact Process for the manufacture of sulphuric acid tended to replace the Lead Chamber Process?

What is the action of concentrated sulphuric acid on (*a*) copper turnings, and (*b*) phosphate rock? *(Delhi H.S. 1964)*

6. (*a*) Give three reactions to show that sulphuric acid acts (*i*) as an oxidising agent and (*ii*) as a dehydrating agent.

(*b*) By what test would you identify that a liquid is sulphuric acid?

(*c*) Mention four important uses of sulphuric acid.
(Nagpur Pre-Univ. 1971)

7. Describe the method of preparation, properties and uses of sodium thiosulphate. *(Delhi H.S. 1970, 63, 61, 60)*

Test Your Understanding

8. Fill in the blanks:

(*a*) In the lead chamber process for the manufacture of ...., the catalyst employed is ..

(*b*) V_2O_5 is used as a.... in the.... of.... acid.

(*c*) When oxalic acid is heated with. ....a mixture of CO and CO_2 is evolved.

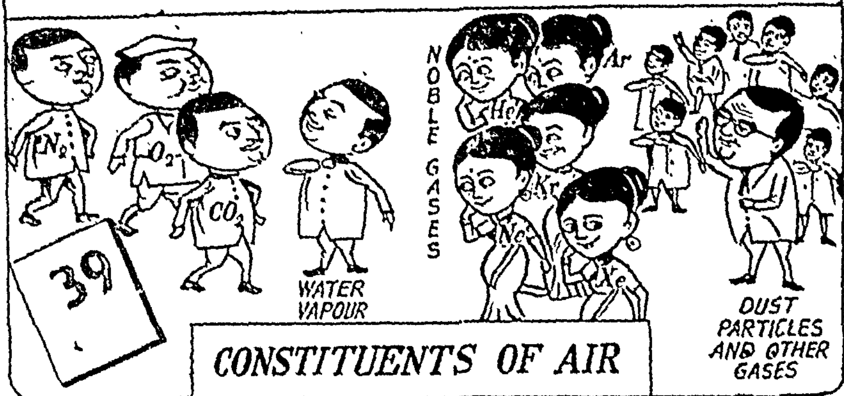
(*d*) H_2SO_4 is. ....agent and......phosphorus to......

(*e*) H_2SO_4 is a.... agent and......cane sugar.

(*f*) Many metals evolve......when heated with conc. H_2SO_4.

KEY

(*a*) H_2SO_4 ; NO_2. (*b*) catalyst ; manufacture ; sulphuric. (*c*) Conc. H_2SO_4. (*d*) an oxidising ; oxidises ; HPO_3 ; (*e*) dehydrating ; chars ; (*f*) SO_2.



The Atmosphere

AIR IS A MIXTURE

1. **Historical.**—The whole envelope of air completely surrounding the earth to a depth of many miles and exerting an average pressure of 14·7 pounds per square inch is termed *atmosphere*. We speak of air only as a limited portion of this envelope. For example, we always speak of a litre of air but never of a litre of atmosphere.

The early Greek alchemists considered air to be one of the four elements—earth, air, fire and water. Priestley, Scheele, Lavoisier and Cavendish showed experimentally in the latter half of the eighteenth century that air is not an element but is a mixture of chiefly nitrogen and oxygen. Noble gases of the atmosphere were discovered only during the last century.

2. **Lavoisier's Experiment on the Composition of Air.**—Lavoisier heated tin with air in a closed vessel and found that increase in weight of tin was equal to the decrease in weight of air and that only a part of air combined with tin. From this he concluded that *air contains at least two constituents, only one of which is absorbed by heated metals.*

Later on he heated mercury in a retort with S-shaped neck dipping under a bell-jar in a trough of mercury (Fig. 39·1). The position of the mercury level was carefully marked on the bell-jar.

He found that more and more red particles were seen floating on the surface of mercury and that the volume of air in contact with mercury decreased from about 50 cubic inches to about 42-43 cubic inches, i.e., about one-sixth of the volume of air was absorbed by heated mercury.

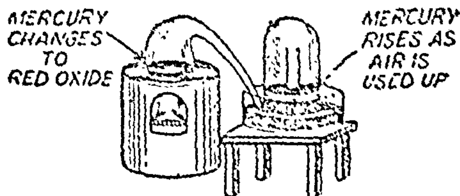


Fig. 39·1—Lavoisier's experiment on the composition of air.

In the air left behind, he found that a burning candle was extinguished and a mouse was quickly suffocated. Lavoisier called this gas *azote*. He further collected the red powder and heated it in a suitable retort and obtained 7-8 cubic inches of a gas in which a smouldering wood splinter burst into flame. This gas had obviously been previously removed from the air by hot mercury. Later on Lavoisier called this gas *oxygen*. In this manner he proved *that air is made up of two gases—oxygen and nitrogen—and that oxygen alone combines with metals on heating.*

3. Composition of Air.—Air is composed of several gases which may be conveniently divided into two groups, *viz.* :

(i) *Constant components.* These include gases like nitrogen, oxygen and noble gases the proportions of which vary but slightly. Carbon dioxide, water vapour and dust particles are also included in the constant components although their proportions vary in different localities at different times.

(ii) *Accidental components* Gases like sulphur dioxide, hydrogen sulphide, ammonia, carbon monoxide and oxides of nitrogen which are present only in traces and are characteristic of a particular locality are called *accidental components.*

An approximate composition of air with functions of the various component gases is given in the table :

Component	Percentage Volume	Percentage Weight	Function
Nitrogen	78·03	75·51	Essential for plant growth directly and animal life indirectly ; serves as a diluent for oxygen in the air.
Oxygen	20 99	23 15	Supports life and combustion Helps oxidation and fermentation.
Carbon dioxide	0·03	0 04	Plant food, used in the synthesis of carbohydrates.
Noble gases	0·95	1·30	
Water vapour	Varies from traces to 2% or more		Supplies moisture for growth of plants and animals ; prevents excessive evaporation from them.
Dust particles			Cause rain by serving as nuclei round which moisture condenses ; cause coloured sunsets.
Other gases			These are H_2S, SO_2, NO_2, O_3 and oxides of nitrogen present in traces only

Expt 1. Take some iron filings in a muslin bag and tie it to the end of a glass rod. Moisten the bag and ... a cylinder placed in a trough of ... wate ... itro- ... jar, ... d to be covered with rust.

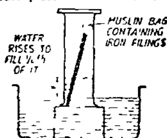


Fig 39 2.

This shows that air is made up of at least two constituents. One of them is used in rusting of iron and is about one-fifth of the volume of air The other is non-supporter of combustion.

Expt. 2. Take some lime water in a dish and blow air through it with the help of a foot bellows. It turns milky showing the presence of carbon dioxide in air

Expt. 3. Put some ice in a glass tumbler and allow it to stand Drops of water are seen on the outer surface of the tumbler. Air in contact with the tumbler gets cooled and the water vapours present in it condense to give water drops.

Expt. 4. Examine a beam of light entering a dark room through a hole. Dust particles will be seen floating in air.

4. **Air is a Mechanical Mixture.**—There is much evidence to show that air a mechanical mixture of its component gases and not a compound. For expample :

(*i*) The composition of air varies from locality to locality, time to time and at different altitudes. If it were a compound, it would always have a definite composition by weight.

(*ii*) Components of air can be readily separated by simple physical methods.

(*iii*) In contact with water, nitrogen and oxygen dissolve independently in the ratio of their solubilities and partial pressures. The two gases are present in the ratio 4 : 1 in the atmosphere and 2 : 1 in the air dissolved in water.

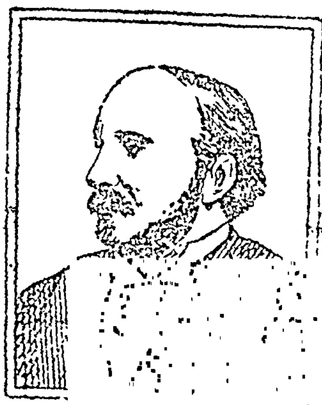
(*iv*) *Properties of air are the average of its component gases.*

(*v*) No energy is evolved or absorbed when a sample of air is obtained by mixing the component gases in proper proportions.

(*vi*) No chemical formula can be assigned to air to represent correctly its percentage composition.

THE NOBLE GASES

5. **Introduction.**—The elements helium, neon, argon, krypton, xenon and radon constitute group zero of the periodic table. Each one of them is characterized by the saturation of its outermost orbit. Since they have no tendency to lend, borrow or share electrons they show no ordinary chemical activity and are known as the noble or inert gases.



Lord Rayleigh
(1842 - 1919)
English physicist ; with Ramsay he discovered the element argon in 1894 and was awarded Nobel Prize for Physics in 1904.



Sir William Ramsay
(1812—1916)
Scottish chemist ; he was awarded Nobel Prize for Chemistry in 1904. With Lord Rayleigh he discovered argon in 1894 and with Travers he discovered neon, krypton and xenon.

6. **Historical.**—Helium was noticed by Sir Norman Lockyer in 1868 in the spectrum of the sun and derives its name from the Greek word "helios" [illegible] Neon (Greek, *neos*=*new*) [illegible] ful fractional distillation [illegible] *ive*) in air was suspected [illegible] Rayleigh and Ramsay in [illegible] (=*Stranger*, Greek) were [illegible] s of liquid air. Radon [illegible] um emanations Ramsay and Gray determined its atomic weight in 1908 and called it niton (Latin, *nitens*=*shining*).

7. **Preparation.**—Helium is prepared from a natural gas which contains up to 2 per cent of helium, by liquefying the other components in liquid air. Argon, krypton and xenon are obtained by fractional distillation of liquid air. Randon and its isotopes are given by the corresponding radioactive elements.

8. **Properties.**—Noble gases are all colourless, odourless and tasteless. These are all monoatomic in the gaseous state as shown by the ratio of their specific heats at constant pressure and constant volume. The ratio $c_p/c_v = 1·67$ in each case and this is the value for monoatomic gases. While their physical constants are given in the table below, they are chemically inactive and give no compounds. Recently however, it has been found possible to prepare a few compounds of them.

Element	At. No.	At wt also Mol. wt.	M Pt.	B Pt.	Density with respect to air	Vol per million vol of air
Helium	2	4·00	−272°C	−269°C	0·14	5
Neon	10	20·2	248·7	−245·9	0·7	18
Argon	18	39·9	−189·1	−185·7	1·34	9,400
Krypton	36	83·7	−157·0	−152·2	2·86	1
Xenon	54	131·3	−140	−109·1	4·5	0·09
Radon	86	222	−71	−61·8	7·6	—

9. **Uses of Noble Gases.**—A variety of uses to which different members are put are .

Helium. (i) For filling balloons and airships. This is due to the fact that helium has a lifting power of 92 per cent that of hydrogen.

(ii) Mixture of helium with oxygen under pressure is supplied to sea-divers for respiration If air were supplied to them, nitrogen present, which is very soluble in blood, would give a painful sensation due to its evaporation as the divers come out. This mixture is also used in the treatment of certain respiratory diseases like asthma.

(iii) In metallurgy where an inert atmosphere is required.

Neon. To produce coloured glow in electric signs which are neon-filled tubes at very low pressure (2 mm.) and glow on the passage of electric discharge through them. Neon mixed with argon or mercury vapours is also used.

Argon. Mixed with 26 per cent nitrogen it is used in gas-filled electric lamps ; also in radio valves and tubes.

Krypton and Xenon have not been prepared in large quantities and as such have not been employed for any useful purpose.

Radon. Used in curing malignant tumours and wounds (*radiotherapy*).

QUESTIONS

Essay-type Questions

1. Describe an experiment to show that air is a mixture of nitrogen and oxygen which are present in the ratio 4 : 1 by volume. What are the other constituents of ordinary air ? How can you demonstrate their presence in it ? (*Punjab H.S. 1962*)

2. Describe Lavoisier's experiments on the composition of air and the inference he drew from them. Describe any laboratory experiment to the same effect which you have seen ?

3. Describe the statement "Air is a mechanical mixture of the component gases, not a chemical compound."

4. Give an account of the discovery of noble gas elements and the uses to which they are put. Discuss the position assigned to them in the Periodic Table.

5. What are the chief constituents of atmosphere ? In what proportion are they found ? Compare and contrast their properties. Give uses of each gas in industry. (*Punjab H.S. 1963*)

6. Name the important members of the noble gases and alkali metal families in the Periodic Table. How do the electronic structures of members of the two families differ ? Can you relate the stability of the noble gases and the extreme reactivity of the alkali metals to the difference in their electronic structures ? (*Punjab Pre-University 1969*)

Test Your Understanding

7. Fill in the blanks :

(*a*) Constituent of air which supports combustion is......and it constitutes......% of air by volume.

(*b*) When air is blown in lime water with foot bellows, it turns milky showing the presence of......in air.

(*c*) Composition of air varies with locality. It shows air is a......not a......

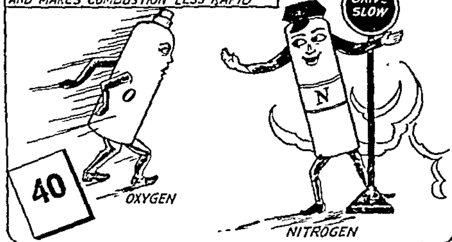
(*d*) Noble gas constitutes the group......of the Periodic Table.

(*e*) The ratio c_p/c_v for noble gases is......showing that these are......

(*f*) Lifting power of......is 92% that of hydrogen. It is used in filling ......and......

KEY

7. (*a*) oxygen, 20·99 ; (*b*) carbon dioxide ; (*c*) mechanical mixture, compound ; (*d*) zero ; (*e*) 1·67, monoatomic gases ; (*f*) helium, balloons, airships.



Nitrogen

1. **Historical.**—Nitrogen was discovered in 1772 by Daniel Rutherford, a Scottish physician and chemist He obtained it by removing carbon dioxide from products of breathing of small animals in closed space. Others who made important contributions towards its discovery were Priestley, Cavendish, Scheele and Lavoisier who proved its elementary nature and called it *azote* (= without life). The present name was derived from *nitre*, well-known nitrogen compound.

2. **Occurrence**—Elementary nitrogen constitutes three-fourths of air by weight or four-fifths by volume It is also abundant in the combined state as saltpetre (KNO_3), sodium nitrate (Chile saltpetre) and ammonium salts. Nitrogen is an essential constituent of all vegetable and animal proteins while fertile soils contain nitrogen as ammonium salts and nitrates.

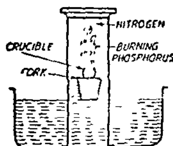


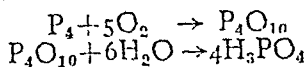
Fig 40 1—Preparation of nitrogen from air.

3. **Preparation of Nitrogen.**

(1) From air. Nitrogen is obtained from air by removing the oxygen present. Different methods employed for the removal of oxygen are :

(i) By burning Phosphorus. A small crucible is placed on a cork floating in water. A small piece of phosphorus is put in the crucible and ignited. The crucible is immediately covered by a

gas jar as shown in Fig. 40·1. Oxygen present in the gas ja combines with the burning phosphorus to form phosphorus pent oxide which dissolves in water leaving behind nitrogen.



$$P_4 + 5O_2 \rightarrow P_4O_{10}$$
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

(ii) **By passing over red hot copper gauze.** Oxyge present in air can also be removed by passing it over red ho copper gauze (Fig. 40·2) Air is bubbled throug potassium hydroxide t remove carbon dioxid and then passing over re hot copper. Oxygen pre sent in air combines wit copper to form coppe oxide and nitrogen co lects in a gas jar of wate

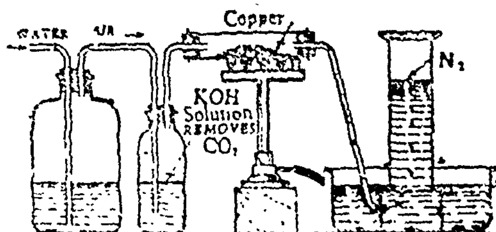


Fig. 40·2—Preparation of nitrogen by removal of oxygen from air by passing it over heated copper.

Several other sub stances, *e.g.*, iron filing steel, wood or carbon can be employed in place of copper gau to remove oxygen from air.

(iii) **By fractional evaporation of liquid air.** Nitroge *required for industrial purposes is manufactured* by fractional evaporation of liquid air (*see* page 2·16).

(2) From Nitrogenous Compounds.

(*i*) **Laboratory method.** Nitrogen is prepared in the laboratory by heating a solution containing equivalent amounts of sodium nitrite and ammonium chloride or sulphate Nitrogen is collected over water as shown in the diagram (Fig. 40·3).

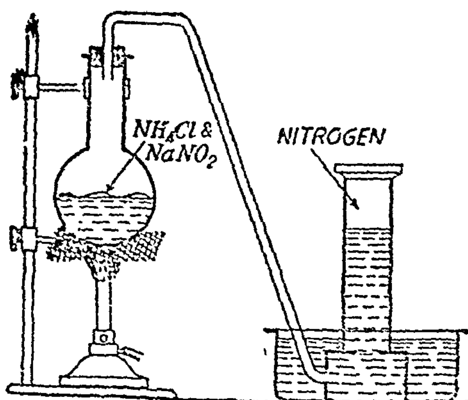
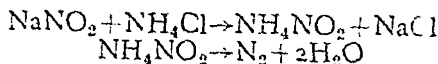
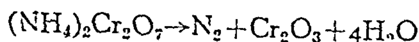


Fig. 40·3—Laboratory preparation of nitrogen.



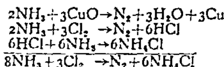
$$NaNO_2 + NH_4Cl \rightarrow NH_4NO_2 + NaCl$$
$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

(*ii*) It may also be obtained in the laboratory by heati gently red crystals of ammonium dichromate. Violent action tak place accompanied by flashes of light when nitrogen is liberat and a green residue of chromic oxide is left behind (*Volca Experiment*).



$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$$

(iii) ... ned by oxidati ... In each case



$$2NH_3+3CuO \rightarrow N_2+3H_2O+3Cu$$
$$2NH_3+3Cl_2 \rightarrow N_2+6HCl$$
$$\underline{6HCl+6NH_3 \rightarrow 6NH_4Cl}$$
$$8NH_3+3Cl_2 \rightarrow N_2+6NH_4Cl$$

Nitrogen obtained from nitrogenous compounds is pure and differs from a sample of nitrogen obtained from air. The latter is not very pure because it contains all the other ingredients of air except oxygen. For example, it contains noble gases of the atmosphere.

4. Properties of Nitrogen.

(*a*) **Physical.** (*i*) It is a colourless, odourless and tasteless gas.

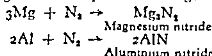
(*ii*) It is slightly lighter than air

(*iii*) It is only slightly soluble in water.

(*iv*) It is not poisonous but animals die in an atmosphere of nitrogen for want of oxygen.

(*v*) It can be liquefied to a colourless liquid (b p. $-195{\cdot}8$°C) which freezes to a white solid (m p. $-209{\cdot}8$°C)

(*b*) **Chemical.** (*i*) Nitrogen is incombustible and a non-supporter of combustion but burning magnesium and aluminium continue burning in an atmosphere of nitrogen forming nitrides.



$$3Mg + N_2 \rightarrow \underset{\text{Magnesium nitride}}{Mg_3N_2}$$
$$2Al + N_2 \rightarrow \underset{\text{Aluminium nitride}}{2AlN}$$

(*ii*) It is a non-supporter of life and neutral towards litmus.

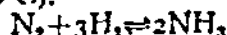
(*iii*) **Combination with elements.** Nitrogen is very inactive and combines with other elements with difficulty. For example :

(*a*) With oxygen it combines only in the presence of lightning discharge or when the mixture is passed through an electric arc.



$$N_2+O_2 \rightleftharpoons 2NO$$

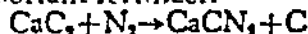
(*b*) With hydrogen it combines under pressure (200--900 atmospheres) and in the presence of a catalyst (finely divided iron+molybdenum at 450°C).



$$N_2+3H_2 \rightleftharpoons 2NH_3$$

(*c*) With metals like magnesium and aluminium it combines only at high temperatures [*see* (*i*) above].

(*iv*) **Combination with Calcium carbide.** On heating calcium carbide (800°C) in a current of nitrogen we get calcium cyanamide, an important fertilizer.



$$CaC_2+N_2 \rightarrow CaCN_2+C$$

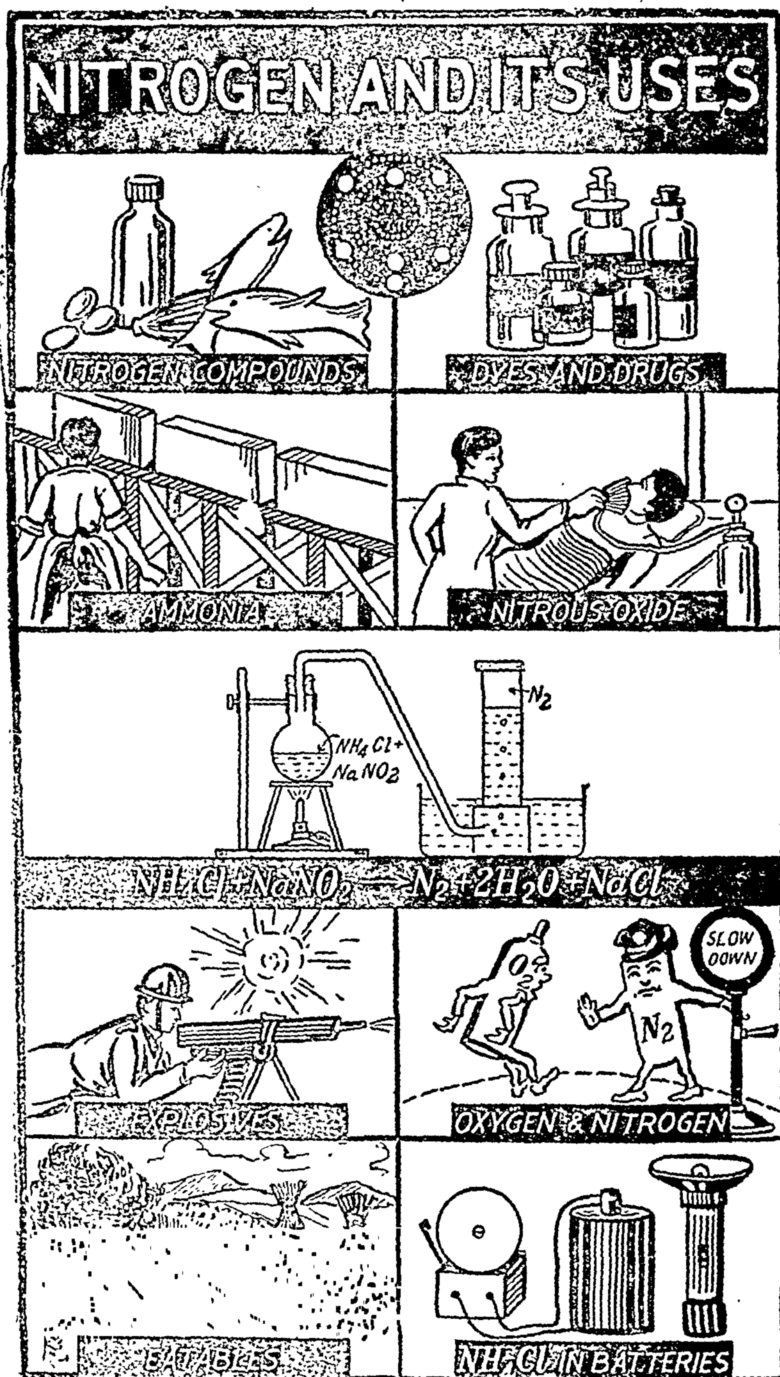

NITROGEN AND ITS USES
NITROGEN COMPOUNDS
DYES AND DRUGS
AMMONIA
NITROUS OXIDE
N_2
$NH_4Cl +$
$NaNO_2$
$NH_4Cl + NaNO_2 \longrightarrow N_2 + 2H_2O + NaCl$
EXPLOSIVES
SLOW DOWN
N_2
OXYGEN & NITROGEN
EATABLES
NH_4Cl IN BATTERIES

Fig. 40·4.

(*v*) Known valencies of nitrogen are negative 3 (e.g. in NH_3 and positive 1, 2, 3, 4 and 5, *e.g.*, in N_2O, NO, N_2O_3, N_2O_4 and N_2O_5 respectively).

Tests. (*i*) Nitrogen is colourless, odourless and tasteless.

(*ii*) It has no action on litmus and lime water.

(*iii*) It is incombustible and non supporter of combustion but magnesium ribbon burns in a jar of nitrogen.

6. **Uses.**—(*i*) Nitrogen serves to dilute the action of oxygen in air and makes combustion much less rapid.

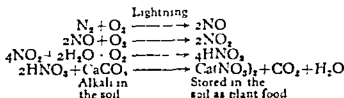
(*ii*) It is used for filling electric lamps and providing an inert atmosphere in certain metallurgical operations.

(*iii*) Large volumes of nitrogen are used in the manufacture of ammonia, nitric acid, calcium cyanamide and other nitrogen compounds.

7. **Nitrogen Cycle**—Nitrogen is an essential constituent of animal and vegetable matter and is indispensable for their growth. Ultimate source of nitrogen is atmospheric nitrogen but neither animals nor plants are capable of assimilating free nitrogen. It is interesting to note how nitrogen passes from atmosphere to plants and animals, converted into useful products i.e. ammonia, nitric acid and calcium cyanamide and still its percentage in the atmosphere *remains practically unchanged. This is due to the fact that combined* nitrogen is constantly passing back to the atmosphere. The cycle of changes involved constitutes what is known as Nitrogen cycle and is outlined on page 2·167.

(1) Conversion of atmospheric nitrogen to plant food in the soil. The conversion is being brought about in a number of ways as given below :

(i) **By lightning.** Nitrogen and oxygen of the air combine to form nitric oxide when lightning discharges occur in the atmosphere. Nitric oxide is oxidised by excess of oxygen present to nitrogen dioxide which further combines with water in the presence of excess c[illegible] This is washed down by rain and [illegible] the soil (limestone, etc.) to form ni[illegible] act as storehouse of plant food.



(*ii*) **By Symbiotic Bacteria.** Most of the crops, *e.g.*, wheat, corn and oats, cannot utilise the free nitrogen of the atmosphere. They are constantly and rapidly removing nitrogen compounds from the soil and assimilating them. Certain other plants (*e.g.*, beans, peas, clover, and alfalfa—Leguminous plants) have small nodules on their roots. A special type of nitrogen-fixing bacteria called *Symbiotic bacteria* thrive in these nodules (Fig. 40·5). These bacteria have the capacity of converting the atmospheric nitrogen into nitrogen compounds which the plants can easily assimilate. A wise farmer always grows one of these crops every three or four years to keep his soil reasonably fertile.

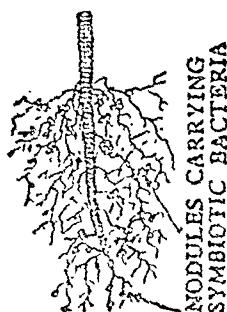


Fig. 40·5—Nitrogen-fixing bacteria grow in the nodules of leguminous plants.

(*iii*) **By other methods.** Large quantities of atmospheric nitrogen are being daily converted into ammonia by Haber's process or Cyanamide process and into nitric acid by Arc process or by oxidation of ammonia by Ostwald process (*see* Fixation of Nitrogen, page 2·167). Ammonia and nitric acid so manufactured are converted into ammonium salts and nitrates which are added to the soil as chemical manures and serve as reservoir of plant food in the soil. Some naturally occurring nitrates like Chile nitre, etc., may also be added.

(2) **Conversion of Nitrogen compounds in the soil into plant and animal proteins.** As the plants grow in the soil, they assimilate the various nitrogen compounds present there through their rootlets. In the body of the plants, under the influence of light these nitrogenous compounds are converted into complex organic compounds called *proteins*.

Plants serve as food for the animals. The plant proteins taken by animals are converted into animal proteins which further break up into urea and amino-acids in their body. Thus the waste products excreted by the animals contain urea and amino-acids.

(3) **Ammonification.** All these complex nitrogenous compounds present in plants, their products, animals or their waste products decay. During the putrefaction the combined nitrogen in them is converted into ammonia or ammonium salts and the bacteria bringing about this change is called *ammonifying bacteria*.

Coal obtained by slow carbonisation of plants under the surface of earth also contains the nitrogenous compounds. When coal is subjected to destructive distillation, ammonia is liberated. This is used for the manufacture of chemical manures, *e.g.*, ammonium sulphate, which are added to the soil.

(4) **Nitrification.** Ammonia and ammonium salts are oxidised in the soil first to nitrites by *nitrosifying bacteria* and then to nitrates by another kind of bacteria present in the soil called

nitrifying bacteria. Nitrites are poisonous to plants but the final product, nitrates, serve as plant food. Thus the nitrogen which the plants get from the soil is returned to the soil *again through ammonification and nitrification.*

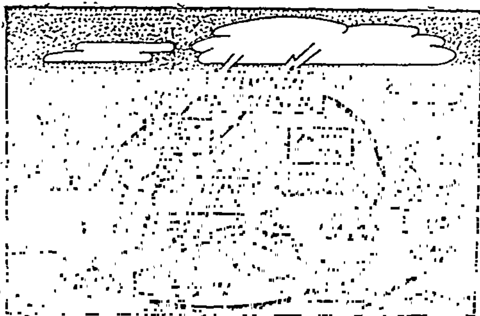


Fig. 40·6—Artist's representation of the nitrogen cycle in nature.

(5) **Denitrification.** Nitrogenous compounds present in the soil are also being constantly decomposed by the action of *denitrifying bacteria.* Thus a part of nitrogen is again being set free and returned to the atmosphere.

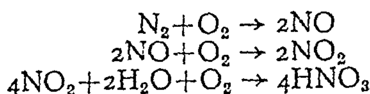
In this way a never-ending cycle of changes known as *nitrogen cycle* is going on in nature. This is summarized in the diagram given on the next page (Fig. 40·7).

8. **Fixation of Nitrogen**.—Nitrogen is an inert element with little chemical activity. Recent investigations have shown that under special conditions it combines with a number of other substances to give nitrogenous compounds. The nitrogen present in the atmosphere is free or elementary nitrogen whereas nitrogen present in various nitrogenous compounds is called *combined or fixed nitrogen.* The *conversion of free atmospheric nitrogen into nitrogen compounds is called* **fixation of nitrogen**.

Methods employed for fixation or bringing atmospheric nitrogen into combination :

(1) **Manufacture of nitric acid (Birkland-Eyde Process).** When air is passed through an electric arc, nitrogen combines with oxygen to give nitric oxide which on cooling combines with

oxygen further to give nitrogen dioxide. This on absorption in water in presence of excess of air gives nitric acid.



$$N_2+O_2 \rightarrow 2NO$$
$$2NO+O_2 \rightarrow 2NO_2$$
$$4NO_2+2H_2O+O_2 \rightarrow 4HNO_3$$

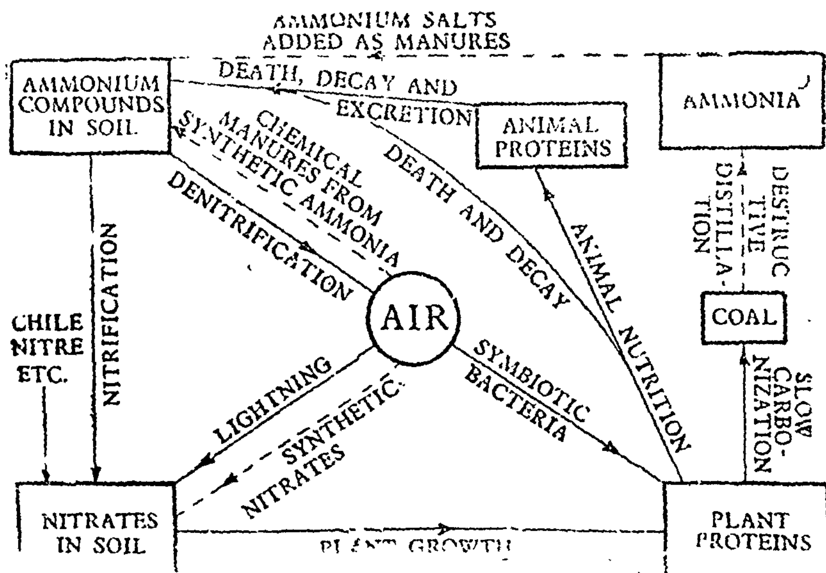
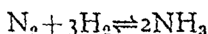


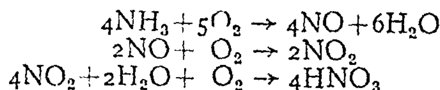
Fig. 40·7—Nitrogen cycle wherein natural changes have been shown by full lines while artificial processes have been depicted by dotted lines.

(2) **Manufacture of ammonia (Haber's Process).** A mixture of nitrogen (manufactured by liquefaction of air) and hydrogen in the ratio 1 : 3 under pressure (200—900 atmospheres) is passed over a catalyst (finely divided iron+molybdenum as promoter) heated to about 500°C.



$$N_2+3H_2 \rightleftharpoons 2NH_3$$

The ammonia so manufactured can be oxidised to nitric oxide by passing a mixture of ammonia (1 vol.) and air (8 vol.) over heated platinum gauze at 800°C. Nitric oxide combines with more of oxygen to give nitrogen dioxide which when absorbed in water in presence of excess of air gives nitric acid (Ostwald's Process).



$$4NH_3+5O_2 \rightarrow 4NO+6H_2O$$
$$2NO+O_2 \rightarrow 2NO_2$$
$$4NO_2+2H_2O+O_2 \rightarrow 4HNO_3$$

Ammonia and nitric acid manufactured above may be converted into ammonium salts and nitrates suitable as fertilizers. Thus these methods of nitrogen-fixation are of vital importance to the agriculturist.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Action of heat on (*i*) Ammonium nitrite, (*ii*) Ammonium dichromate.

2. Ammonia+(*i*) Cupric oxide, (*ii*) Chlorine, (*iii*) Catalytic oxidation.

3. Nitrogen+(*i*) Oxygen, (*ii*) Hydrogen, (*iii*) Calcium carbide, (*iv*) Magnesium or Aluminium.

4. Nitric oxide+Oxygen.

5. Nitrogen dioxide+Water+Oxygen.

QUESTIONS

Essay-type Questions

1. How and under what conditions does nitrogen react with the following : (*a*) Hydrogen, (*b*) Oxygen, (*c*) Calcium carbide, (*d*) Magnesium ? What is the action of water on the product formed in each case ?

2. How does atmospheric nitrogen differ from chemical nitrogen ? Give in brief one method of preparing a sample of each ?

3. Explain what is meant by Nitrogen cycle in nature ? (*Punjab Pre-Univ. 1970*)

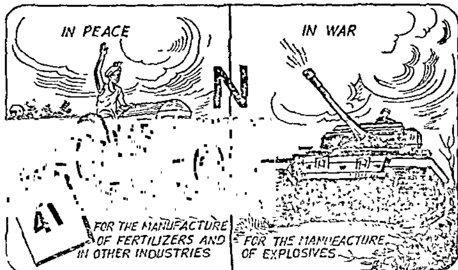
4. What do you understand by the term fixation of nitrogen ? Give a brief but clear account of the methods employed for bringing atmospheric nitrogen into combination. Why is the importance of nitrogen in industry increasing ? (*Punjab H.S. 1961 ; Punjab Pre-Univ. 1962 ; Delhi Pre-Medical 1963*)

Test Your Understanding

5. Fill in the blanks :
   (*a*) Main constituent of air is .....and it......combustion.
   (*b*) When $(NH_4)_2Cr_2O_7$ is heated......is evolved.
   (*c*) On heating a solution containing NH_4Cl and......nitrogen is evolved.
   (*d*) When N_2 is passed over......, nitrolim is formed.
   (*e*) Haber's process is a method of......of atmospheric nitrogen and is used in the manufacture of......
   (*f*) Mg burns in N_2 forming......

KEY

(*a*) N_2 ; does not support ; (*b*) N_2 ;
(*c*) $NaNO_2$; (*d*) heated CaC_2 ;
(*e*) fixation ; NH_3 ; (*f*) Mg_3N_2.



Ammonia

1. Historical.—Ammonia was known to the early chemists. It was originally prepared by heating certain organic substances like hoofs and horns and the water solution of the gas was called *spirits of hartshorn*. Priestley, in 1774, prepared the gas by heating sal ammoniac with lime and collected it over mercury. Berthollet in 1785 and Davy in 1800 established its composition.

2. **Occurrence.**—Traces of ammonia occur in air and natural waters. It is produced in nature by the action of purifying and ammonifying bacteria on organic matter, *e.g.*, in stables and cattle barns.

3. **Preparation of Ammonia in the Laboratory.**—(i) Ammonia is prepared in the laboratory by heating ammonium chloride with slaked lime (in the ratio 1 : 3) in a hard glass test tube (Fig. 41·1). The gas evolved is dried by passing through a tower packed with quicklime and collected by downward displacement of air as shown. The gas being very soluble in water cannot be collected over water. It can, however, be collected over mercury.

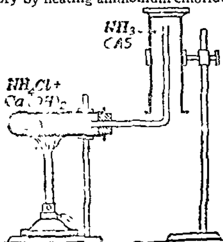
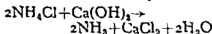


Fig. 41·1—Preparation of ammonia gas



$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

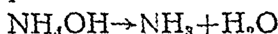
It reacts with sulphuric acid forming ammonium sulphate. With calcium chloride it gives a complex compound of the formula $CaCl_2.8NH_3$. With phosphorus pentoxide also it reacts chemically.



$$P_4O_{10} \xrightarrow{2H_2O} 4HPO_3 \xrightarrow{4NH_3} 4NH_4PO_3$$

Hence sulphuric acid, calcium chloride or phosphorus pentoxide cannot be used for drying ammonia.

(*ii*) It can, however, be conveniently obtained in the laboratory by heating some liquor ammonia.



$$NH_4OH \rightarrow NH_3 + H_2O$$

4. **Manufacture of Ammonia.**

(*i*) **From Ammoniacal Liquor.** Coal gas manufactured by the destructive distillation of coal is cooled and bubbled through water where ammonium salts accompanying coal gas are dissolved. The concentrated solution of ammonium salts so obtained is called ammoniacal liquor. Milk of lime is added to the ammoniacal liquor and steam blown through the mixture. The mixture of steam and ammonia evolved is bubbled through sulphuric acid. Ammonium sulphate thus formed is crystallized out. It is largely used as a fertilizer.



$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

To get liquor ammonia, ammonia evolved is purified and bubbled through water under pressure when a concentrated solution of ammonia is obtained.

(*ii*) **By Haber's Process.** Large quantities of ammonia are manufactured by direct union of the elements by the *Haber's Process.*



Fritz Haber
(1868—1935)
German chemist. He is well known for the synthetic method for the manufacture of ammonia. He won Nobel Prize for Chemistry in 1918.

Theory. Nitrogen and hydrogen combine according to the equation.



$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22{,}400 \text{ cal.}$$

The reaction is reversible, exothermic and proceeds with a decrease in volume. According to Le Chatelier's principle, favourable conditions for maximum yield are :

(*i*) *Low temperature.* Optimum temperature for the reaction has been experimentally found to be 450—500°C.

(*ii*) *High pressure* of the order of 200—900 atmospheres.

(*iii*) To increase the reaction velocity, use of a catalyst (finely divided iron + molybdenum as promoter) is essential.

In Germany a pressure of 200 atmospheres was employed at 450 - 500°C when the yield was 15 per cent. This increased to 40 per cent in the French Claude Process wherein a pressure of about 900 atmospheres was employed at the same temperature.

(*iv*) Impure gases poison the catalyst ; hydrogen and nitrogen used, therefore, must be very pure.

Process. A diagrammatic sketch of the plant employed is shown in Fig. 41·2. Nitrogen obtained by liquefaction of air is mixed with 3 times its volume of pure dry hydrogen and compressed to 200—900 atmospheres pressure. The compressed mixture is passed over the catalyst maintained at about 450—500°C in an electrically heated chamber. The issuing gases containing about 15—40% of ammonia are passed through a condenser when ammonia condenses while the residual gases are recirculated over the catalyst under pressure with the help of an air circulation pump.

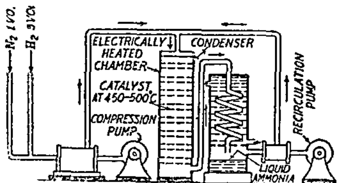
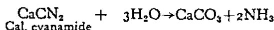


Fig. 41·2—Haber's Process for the manufacture of ammonia

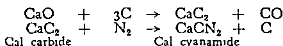
This is the cheapest and the most important method today for the manufacture of ammonia.

(iii) Cyanamide Process. Hydrolysis of calcium cyanamide with superheated steam at 180° C is another important method for the manufacture of ammonia.



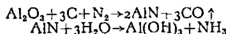
$$\underset{\text{Cal. cyanamide}}{CaCN_2} + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

Calcium carbide is manufactured by heating lime and coke mixture in an electric furnace. It is crushed and heated to 800—1000°C in a current of nitrogen obtained from liquid air and when calcium cyanamide is obtained.



$$CaO + 3C \rightarrow CaC_2 + CO$$
$$\underset{\text{Cal carbide}}{CaC_2} + N_2 \rightarrow \underset{\text{Cal cyanamide}}{CaCN_2} + C$$

(iv) As a by-product. In the purification of bauxite by Serpek's Process, ammonia is obtained as a by-product. Bauxite is mixed with coke and heated in a current of nitrogen and the aluminium nitride so formed is hydrolysed with water.



$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO\uparrow$$
$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

5. **Properties of Ammonia**—(a) **Physical**. (i) Ammonia is a colourless gas with a characteristic pungent odour and an alkaline taste. It brings tears into the eyes.

(ii) It is lighter than air and is collected, therefore, by the downward displacement of air.

(*iii*) It is extremely soluble in water. One volume of water dissolves 1300 volumes of ammonia at 0°C and 760 mm.

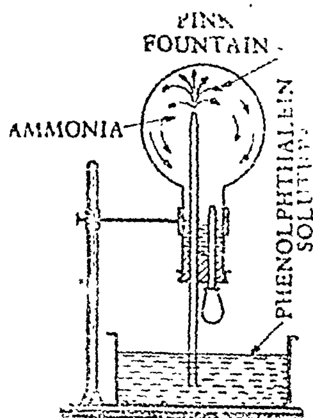


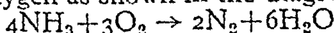
Fig. 41·3—Fountain Experiment.

Fountain Expt. Fill a round-bottom flask with dry ammonia gas and fit it as shown in Fig. 41·3. Dip the jet tube in phenolphthalein solution and introduce a little water in the flask with the help of a dropper. Water inside dissolves ammonia gas creating a partial vacuum there. Phenolphthalein solution is pushed up by the atmospheric pressure and a red fountain works inside the flask.

(*iv*) It liquefies when cooled under pressure to a colourless liquid (b.p. —33·4°). Liquid ammonia freezes to white snowy crystals (m.p. —78°C).

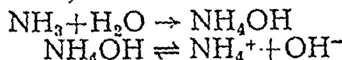
(*v*) Latent heat of vaporization of ammonia is 330 calories. It is, therefore, extensively used in ice-plants for refrigeration.

(*b*) **Chemical :** (*i*) **Combustion.** Ammonia is ordinarily neither combustible nor a supporter of combustion. A jet of ammonia can, however, be made to burn in an atmosphere of oxygen as shown in the diagram (Fig. 41·4).



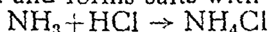
$$4NH_3+3O_2 \rightarrow 2N_2+6H_2O$$

(*ii*) **Basic Nature.** Ammonia gas dissolves in water to give ammonium hydroxide, a base which ionizes to give hydroxyl ions in solution.



$$NH_3+H_2O \rightarrow NH_4OH$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Thus ammonia gives the reactions of a typical base, *e.g.*, it turns red litmus blue, phenolphthalein solution pink and forms salts with acids.



$$NH_3+HCl \rightarrow \underset{\text{Thick white fumes}}{NH_4Cl}$$



$$2NH_3+H_2SO_4 \rightarrow (NH_4)_2SO_4$$

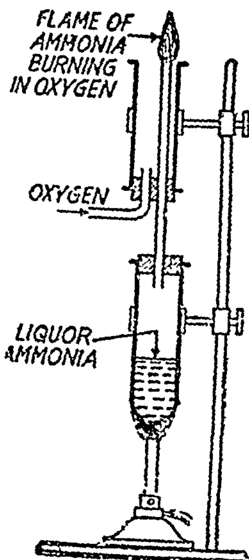
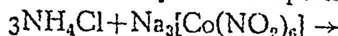


Fig. 41·4—A jet of ammonia burning in oxygen.

(*iii*) **Ionic reactions.** An aqueous solution of ammonia contains ammonium and hydroxyl ions as given above. The solution gives, therefore, the reactions of both these ions as given below :

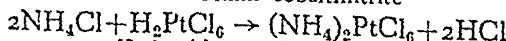
(*a*) **Reactions of Ammonium ions.** In a neutral solution, it gives a yellow precipitate of ammonium cobaltinitrite with sodium cobaltinitrite solution and yellow crystalline precipitate of ammonium chloroplatinate with hydrochloroplatinic acid.



$$3NH_4Cl+\underset{\text{Sod. cobaltinitrite}}{Na_3[Co(NO_2)_6]} \rightarrow$$

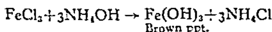


$$\underset{\text{Amm. cobaltinitrite}}{(NH_4)_3[Co(NO_2)_6]}+3NaCl$$

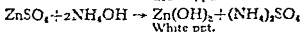


$$2NH_4Cl+\underset{\text{Hydrochloroplatinic acid}}{H_2PtCl_6} \rightarrow \underset{\text{Amm. Chloroplatinate}}{(NH_4)_2PtCl_6}+2HCl$$

(b) Reactions of Hydroxyl ions. It reacts with certain metallic salts and precipitates hydroxides of the metals. For example,

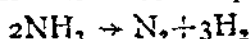


$$FeCl_3 + 3NH_4OH \rightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3} + 3NH_4Cl$$



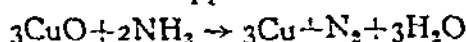
$$ZnSO_4 + 2NH_4OH \rightarrow \underset{\text{White ppt.}}{Zn(OH)_2} + (NH_4)_2SO_4$$

(iv) Dissociation. Ammonia decomposes into nitrogen and hydrogen at red heat or when electric sparks are passed through it.



$$2NH_3 \rightarrow N_2 + 3H_2$$

(v) Oxidation. We have already seen that a jet of ammonia burns in oxygen when it is oxidised to nitrogen. It is also oxidised when passed over heated copper oxide.



$$3CuO + 2NH_3 \rightarrow 3Cu + N_2 + 3H_2O$$

It is oxidised to nitric oxide when a mixture of ammonia and air is passed over heated platinum guaze (*catalyst*) at 800°C.



$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

[illegible] heard and the spiral begins to glow. Reddish brown fumes of nitrogen dioxide are produced

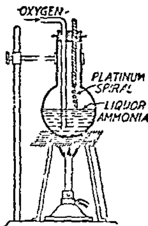
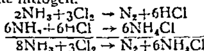


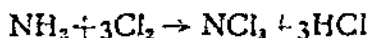
Fig 41 5—Catalytic oxidation of ammonia

(vi) Action of halogens. Both chlorine and bromine oxidise ammonia and liberate nitrogen.



$$\begin{array}{l} 2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl \\ \underline{6NH_3 + 6HCl \rightarrow 6NH_4Cl} \\ 8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl \end{array}$$

With excess of chlorine, nitrogen trichloride, an explosive substance, is formed.



$$NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$$

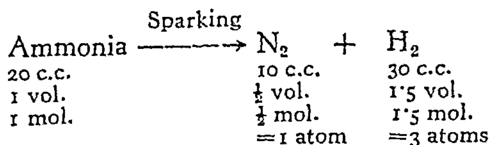
Iodine flakes when rubbed with liquor ammonia give a dark brown precipitate of nitrogen iodide, $NH_3 \cdot NI_3$. This explodes readily on drying (*see* page 2·82).

(vii) Formation of complex compounds Ammonia reacts with many metallic salts forming soluble complexes. For example:

(a) Copper sulphate when treated with ammonium hydroxide gives a blue precipitate of copper hydroxide which dissolves further forming cupri-ammine sulphate, $Cu(NH_3)_4SO_4$—a soluble complex with deep blue colour.

(b) White precipitate of silver chloride is dissolved in ammonia due to the formation of silver ammine chloride, $Ag(NH_3)_2Cl$, a soluble complex.

Thus we learn that 10 c.c. of nitrogen and 30 c.c. of hydrogen are obtained by sparking 20 c.c. of ammonia. Or 1 vol. of ammonia gives on sparking $\frac{1}{2}$ vol. of nitrogen along with 1·5 vol. of hydrogen.

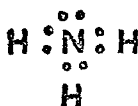


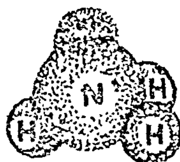
$$\text{Ammonia} \xrightarrow{\text{Sparking}} N_2 + H_2$$

Ammonia	N_2	H_2
20 c.c.	10 c.c.	30 c.c.
1 vol.	$\frac{1}{2}$ vol.	1·5 vol.
1 mol.	$\frac{1}{2}$ mol.	1·5 mol.
	=1 atom	=3 atoms

Applying Avogadro's law to this, we find that 1 molecule of ammonia gives $\frac{1}{2}$ molecule (=1 atom) of nitrogen along with 1·5 molecules (=3 atoms) of hydrogen, *i.e.*, molecular formula of ammonia is NH_3.

This is further confirmed by its vapour density data which gives the molecular weight of ammonia as 17 and which corresponds to the formula, NH_3.

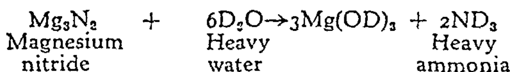




(*a*) Fig. 41·8. (*b*)

9. **Structure of Ammonia Molecule.**—The bonds between N and H atoms are covalent bonds inclined at an angle of 108°. In Fig. 41·8, (*a*) gives the electronic formula while (*b*) gives the arrangement and the relative sizes of the atoms.

10. **Heavy Ammonia.**—Heavy ammonia is prepared by treating magnesium nitride with heavy water.



$$\underset{\text{Magnesium nitride}}{Mg_3N_2} + \underset{\text{Heavy water}}{6D_2O} \rightarrow 3Mg(OD)_2 + \underset{\text{Heavy ammonia}}{2ND_3}$$

It is a gas resembling ordinary ammonia in smell but differs from it in other physical properties. It is 1·174 times as heavy as ordinary ammonia.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Ammonium chloride+Slaked lime.
2. Calcium cyanamide+Steam.
3. Calcium carbide+Nitrogen.
4. Bauxite+coke (heated in a current of nitrogen).
5. Aluminium nitride+Water.
6. Ammonium chloride+ (*i*) Sodium cobaltinitrite, (*ii*) H platinic acid.
7. Ammonia+(i) Heated copper oxide, (*ii*) Mixed with air over heated platinum gauze, (*iii*) Chlorine, (*iv*) Sodium or potassiu chloride, (*vi*) Copper sulphate, (*vii*) Calcium chloride.

QUESTIONS

Essay-type Questions

1. How is dry ammonia prepared in the laboratory ? Give it properties and tests. (*Punjab Pre-Univ. 1964 ; Punjab* *U. P.*

2. Describe the Haber's process for the manufacture of ammonia. What are the conditions for a good yield ? How may ammonia be converted into nitric acid ? Mention some of the industrial applications of these two compounds. *(Punjab Inter. 1961 ; U.P. Board 1971 ; All India H.S. 1966 ; Punjab Pre-Univ. 1962, 69 ; Delhi H.S. 1972, 67, 60)*

3. How is ammonia manufactured and how is it converted into nitric acid ? What is the action of ammonia on : (*a*) Red hot copper oxide, (*b*) Silver chloride, (*c*) Nessler's solution, and (*d*) Chlorine ? *(Delhi H.S. 1965 ; Bihar 1960)*

4. Describe an important method for the manufacture of ammonia. Give its properties and uses. How does it differ from phosphine ? *(Delhi H.S. 1971, 66, 62)*

5. Describe the manufacture of ammonia by Haber process. Give its uses. How does ammonia react with copper sulphate, chlorine, sodium and ferric chloride ? Give equations. *(All India H.S. 1968)*

6. How is ammonia prepared on a commercial scale ? How is its composition determined volumetrically ? What happens when it reacts with (*a*) silver nitrate solution, (*b*) ferric chloride solution ? *(Delhi H.S. 1969)*

[illegible] few drops of strong
ter the vigorous reac-
residual gas, nitro-
Use the above data

8. How would you remove moisture from ammonia gas ? What is the *action of chlorine on ammonia ? Give the analytical importance of ammonium* hydroxide.

9. (*a*) Why ammonia cannot be dried by passing through sulphuric acid, fused calcium chloride or phosphorus pentoxide ?

(*b*) How would you obtain nitrogen from ammonia and *vice versa* ? *(Punjab Inter. 1965)*

10. (*a*) Give a method for determining the composition of ammonia *(Nagpur Pre-Univ. 1970)*

(*b*) 20 c c. of ammonia gas was enclosed in a eudiometer tube and exploded. The volume after explosion was 40 c c To this 45 c.c of oxygen was added and the mixture again exploded On cooling the volume of the residual gases was found to be 40 c c. Calculate the formula of ammonia.

Test Your Understanding

11. Fill in the blanks in the following :

(i) .. .. and . cannot be used in the drying ammonia gas since they *react with it chemically forming . and . respectively*

(ii) Favourable conditions for the manufacture of ammonia by Haber's process are temperature, . pressure and presence of a catalyst and .. . as promoter.

(iii) With Nessler's reagent ammonia gives . or

(iv) In ammonia molecule N—H bonds are inclined at an angle of .....

(v) Which precipitate of silver chloride dissolves in ammonia due to the formation of . ...or... .

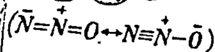
(vi) With copper sulphate solution, ammonia gives a blue precipitate which dissolves in excess giving a deep blue solution of the complex . having the formula. ...

KEY

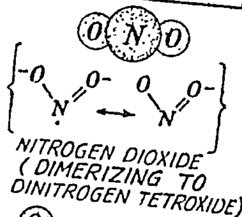
(i) $CaCl_2$; P_4O_{10}, $CaCl_2 8NH_3$, NH_4PO_4 ; (ii) low, high, finely divided iron, molybdenum ; (iii) a reddish brown precipitate ; coloration , (iv) bonds, 108° ; (v) $Ag(NH_3)_2Cl$, complex ; (vi) Tetra-ammine Copper Sulphate, $Cu(NH_3)_4 SO_4$.

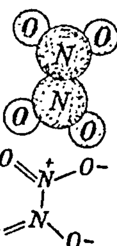
OXIDES OF NITROGEN

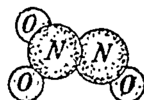
42

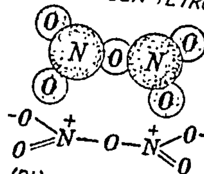











Oxides of Nitrogen

1. **Introduction.**—The important and common oxy-acids of nitrogen are :

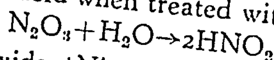
(*i*) Nitrous acid, HNO_2, (*ii*) Nitric acid, HNO_3

Five known oxides of nitrogen are :

(*i*) Nitrous oxide or Laughing gas, N_2O.

(*ii*) Nitric oxide or Nitrous fumes, NO.

(*iii*) Nitrogen trioxide, N_2O_3. It is also called nitrous anhydride as it gives nitrous acid when treated with water.



$$N_2O_3 + H_2O \rightarrow 2HNO_2$$

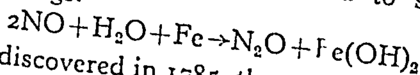
(*iv*) Nitrogen tetroxide⇌Nitrogen dioxide ($N_2O_4 \rightleftharpoons 2NO_2$). It is the mixed anhydride of nitrous and nitric acids.

(*v*) Nitrogen pentoxide, N_2O_5 or Nitric anhydride.

The oxides are closely related to the two common acids and furnish a beautiful example of the law of multiple proportions.

ITROUS OXIDE, N_2O

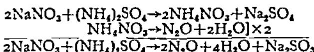
2. **Historical.**—Priestley noticed the formation of nitrous xide in 1722 when nitric oxide was allowed to stand in contact ith moist iron filings.



$$2NO + H_2O + Fe \rightarrow N_2O + Fe(OH)_2$$

Berthollet discovered in 1785, the method for preparing pure s by heating ammonium nitrate. Davy studied its physiological tion and assigned a formula to it.

3. Preparation. (*i*) Nitrous oxide is conveniently prepared ... nitrate or better still by ... ammonium sulphate or ... is liable to explode if



$$2NaNO_3+(NH_4)_2SO_4 \rightarrow 2NH_4NO_3+Na_2SO_4$$
$$NH_4NO_3 \rightarrow N_2O+2H_2O] \times 2$$
$$\overline{2NaNO_3+(NH_4)_2SO_4 \rightarrow 2N_2O+4H_2O+Na_2SO_4}$$

It is collected over hot water (Fig. 42·1) as the gas is fairly soluble in cold water. It may be freed from higher oxides of nitrogen which are invariably present by passing through ferrous sulphate solution. Chlorine (derived from ammonium chloride in ammonium nitrate) and any nitric acid vapours are removed with caustic soda solution. The gas is finally freed from water vapour by bubbling through concentrated sulphuric acid.

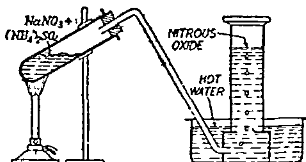
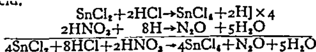


Fig. 42·1—Preparation of nitrous oxide in the laboratory.

(*ii*) ... reduction of nitric acid ... acid. A mixture of ... s heated with a little ...



$$SnCl_2+2HCl \rightarrow SnCl_4+2H] \times 4$$
$$2HNO_3+ \quad 8H \rightarrow N_2O \; +5H_2O$$
$$\overline{4SnCl_2+8HCl+2HNO_3 \rightarrow 4SnCl_4+N_2O+5H_2O}$$

4. **Properties of Nitrous Oxide.**

(*a*) **Physical.** (*i*) It is a colourless gas with faint sweet odour and taste.

(*ii*) It is about 1·5 times as heavy as air.

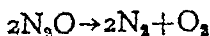
(*iii*) ... cold water, more in alcohol but ... er. That is why nitrous oxide is ...

(*iv*) It can be easily liquefied at 20°C by a pressure of 50 atmospheres to a colourless mobile liquid (b.p. −88·7°C), which can be solidified in liquid air to a snow-white solid (m p. −90·8°C).

(*v*) It is poisonous in nature. When inhaled in small quantities, it produces hysterical laughter (it used to be called 'laughing gas'). Mixed with oxygen it is used as an anaesthetic. Large doses might prove fatal.

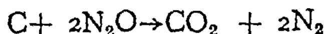
(*b*) **Chemical.** (*i*) It is neutral towards litmus.

(*ii*) **Decomposition.** At ordinary temperature, it is stable but decomposes on heating into nitrogen and oxygen. Decomposition begins at 520°C and is complete at 900°C. It is also decomposed by electric sparks.

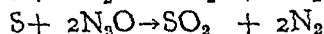


$$2N_2O \rightarrow 2N_2 + O_2$$

(*iii*) **Supporter of Combustion.** It is incombustible but due to its ready decomposition it supports the combustion of a glowing splinter, burning phosphorus and sulphur.



$$C + 2N_2O \rightarrow CO_2 + 2N_2$$



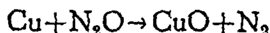
$$S + 2N_2O \rightarrow SO_2 + 2N_2$$



$$P_4 + 10N_2O \rightarrow P_4O_{10} + 10N_2$$

In each case the burning body decomposes the gas, combines with the oxygen and leaves nitrogen as a residue. Feebly burning sulphur is, however, extinguished in nitrous oxide, probably as the temperature is not high enough to decompose nitrous oxide (*Distinction from oxygen*).

(*iv*) **Reduction.** Just like other oxides of nitrogen nitrous oxide when passed over red hot copper is reduced to nitrogen.



$$Cu + N_2O \rightarrow CuO + N_2$$

5. **Uses.**—Mixed with oxygen, it is used as anaesthetic for small-scale operations in dentistry and surgery.

6. **Tests.**—(*i*) Characteristic sweetish smell.

(*ii*) Supports the combustion of glowing splinter, etc.

(*iii*) No coloured fumes are produced with nitric oxide.

7. **Comparison of the Properties of Nitrous Oxide with those of Oxygen.**

(*a*) **Points of resemblance :**

(*i*) Both are colourless.

(*ii*) Both are supporters of combustion.

(*iii*) Both give oxides as products of combustion.

(*b*) **Points of difference :**

(*i*) Nitrous oxide is heavier and more soluble in water than oxygen.

(*ii*) Nitrous oxide has faint sweet smell while oxygen is odourless.

(*iii*) When substances burn in nitrous oxide there is no decrease in volume as in oxygen.

(*iv*) With nitric oxide, oxygen gives red fumes of nitrogen dioxide while nitrous oxide does not.

(v) Nitrous oxide is poisonous and causes insensibility while oxygen supports life.

(vi) Oxygen is soluble in pyrogallic acid while nitrous oxide is not.

(vii) Nitrous oxide is more easily liquefied than oxygen.

8. **Formula of Nitrous Oxide.**—The apparatus used is [illegible] (Fig. [illegible]). It consists of two glass tubes [illegible] and partly [illegible] n is fitted with a rubber cork carrying two delivery tubes fitted with stop-cocks and two copper wires provided with a spoon and platinum wire at their lower end as shown.

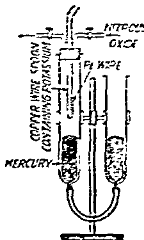


Fig. 42·2—Determination of the formula of nitrous oxide.

[illegible] is equalised. Now electric current is passed through copper wires, potassium catches fire and burns in nitrous oxide when it combines with oxygen leaving behind nitrogen. *On cooling no change in volume is noticed.*

This shows that one volume of nitrous oxide on decomposition gives one volume of nitrogen.

Applying Avogadro's law, we conclude that one molecule of nitrous oxide on decomposition gives one molecule (2 atoms) of nitrogen.

Or one molecule of nitrous oxide is made up of two atoms of nitrogen in addition to some atoms of oxygen (say, x), *i.e.*, the molecular formula is N_2O_x with molecular weight $=28+16x$.

Its vapour density has been experimentally found to be 22, whence its molecular weight $=2\times22=44$.

Equating the two molecular weights, we have

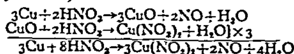
$$28+16x=44 \qquad \text{whence } x=1$$

$\therefore$ Molecular formula of nitrous oxide is N_2O.

NITRIC OXIDE, NO

9. Historical.—J.B. van Helmont seems to have known the gas as early as 1600; Mayow prepared it in 1669 by the action of nitric acid on iron but Priestley (1772) is regarded the real discoverer of nitric oxide as a definite new compound.

10. **Preparation.**—(i) By the action of dilute nitric acid on copper (*Laboratory Method*).



$$3Cu+2HNO_3 \rightarrow 3CuO+2NO+H_2O$$
$$[CuO+2HNO_3 \rightarrow Cu(NO_3)_2+H_2O]\times3$$
$$3Cu+8HNO_3 \rightarrow 3Cu(NO_3)_2+2NO+4H_2O$$

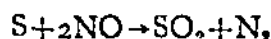
(*b*) **Chemical.** (*i*) It is neutral towards litmus.

(*ii*) **Decomposition.** It is one of the most stable oxides of nitrogen. On heating decomposition begins at 500°C and is still slight at 900°C.



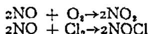
$$2NO \rightleftharpoons N_2 + O_2$$

(*iii*) **Supporter of Combustion.** It is incombustible and supports the combustion of only boiling sulphur and vigorously burning phosphorus. Burning sulphur and feebly burning phosphorus are extinguished. Red hot iron wire burns in nitric oxide.



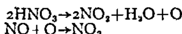
$$S + 2NO \rightarrow SO_2 + N_2$$

R P ctly with oxy- With chlorine

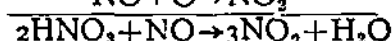


$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO + Cl_2 \rightarrow 2NOCl$$

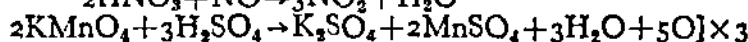
On account of this ready oxidation, it acts as a reducing



$$2HNO_3 \rightarrow 2NO_2 + H_2O + O$$
$$NO + O \rightarrow NO_2$$



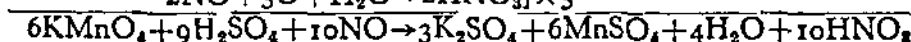
$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O$$



$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O] \times 3$$

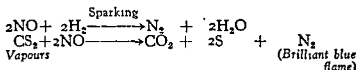


$$2NO + 3O + H_2O \rightarrow 2HNO_3] \times 5$$



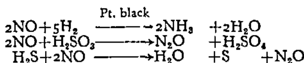
$$6KMnO_4 + 9H_2SO_4 + 10NO \rightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$$

(*v*) **Oxidising Properties.** Whenever nitric oxide is acting as an oxidising agent it is usually reduced to nitrogen but occasionally ammonia or nitrous oxide are also formed.



$$2NO + 2H_2 \xrightarrow{\text{Sparking}} N_2 + 2H_2O$$
$$CS_2 + 2NO \longrightarrow CO_2 + 2S + N_2$$

Vapours *(Brilliant blue flame)*



$$2NO + 5H_2 \xrightarrow{\text{Pt. black}} 2NH_3 + 2H_2O$$
$$2NO + H_2SO_3 \longrightarrow N_2O + H_2SO_4$$
$$H_2S + 2NO \longrightarrow H_2O + S + N_2O$$

(*vi*) **With Ferrous Sulphate.** It combines with ferrous sulphate to give ($FeSO_4.NO$) a dark coloured substance.

12. **Uses.**—(*i*) In the manufacture of nitric acid.

(*ii*) In the detection of oxygen to distinguish it from nitrous oxide.

(*iii*) As a catalyst in the Lead Chamber Process for the manufacture of sulphuric acid.

13. **Tests.**—(*i*) Colourless, (*ii*) Gives brown fumes with air.

Copper chips are placed in a Woulfe's bottle and some water added. The apparatus is fitted as shown (Fig. 42·3). Concentrated nitric acid is poured through the thistle funnel and the nitric oxide liberated is collected over water.

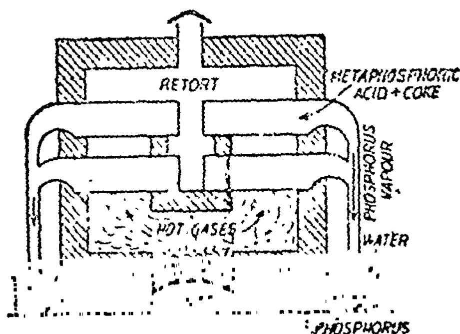
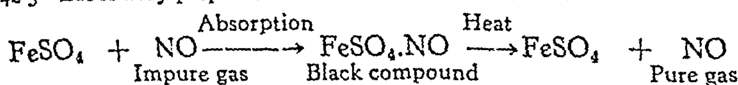


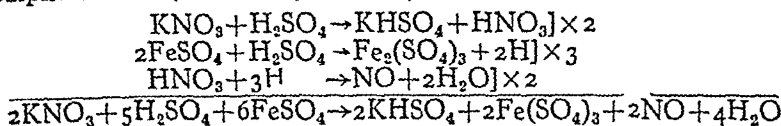
Fig. 42·3—Laboratory preparation of nitric oxide.

The gas is purified by absorbing it in ferrous sulphate solution and heating the black nitrosoferrous sulphate obtained when pure nitric oxide is liberated.



$$\underset{}{FeSO_4} + \underset{\text{Impure gas}}{NO} \xrightarrow{\text{Absorption}} \underset{\text{Black compound}}{FeSO_4.NO} \xrightarrow{\text{Heat}} FeSO_4 + \underset{\text{Pure gas}}{NO}$$

(*ii*) A pure sample of gas is obtained by the reduction of potassium nitrate by heating with ferrous sulphate acidified with sulphuric acid (*Laboratory Method*).



$$\begin{aligned} KNO_3+H_2SO_4 &\rightarrow KHSO_4+HNO_3]\times 2 \\ 2FeSO_4+H_2SO_4 &\rightarrow Fe_2(SO_4)_3+2H]\times 3 \\ HNO_3+3H &\rightarrow NO+2H_2O]\times 2 \\ \hline 2KNO_3+5H_2SO_4+6FeSO_4 &\rightarrow 2KHSO_4+2Fe(SO_4)_3+2NO+4H_2O \end{aligned}$$

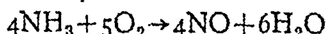
Ferrous chloride acidified with hydrochloric acid can be used in place of ferrous sulphate acidified with sulphuric acid.

(*iii*) By passing air through an electric arc when nitrogen and oxygen of the air directly combine to give nitric oxide (*Commercial Method*).



$$N_2+O_2 \rightleftharpoons 2NO$$

(*iv*) By catalytic oxidation of ammonia by passing a mixture of ammonia (*1 vol.*) and air (*8 vol.*) over heated platinum gauze at 800°C (*Commercial Method*).



$$4NH_3+5O_2 \rightarrow 4NO+6H_2O$$

11. Properties of Nitric Oxide.

(*a*) **Physical.** (i) It is a colourless gas, slightly heavier than air.

(*ii*) In contact with air, it at once gives reddish brown fumes of nitrogen dioxide. It is not possible, therefore, to describe its smell or physiological action.

(*iii*) It is very sparingly soluble in water.

(*iv*) It is liquefied with great difficulty under high pressure at low temperature. Liquid nitric oxide (b.p. −151°C) is colourless in the absence of air and solidified to a white solid (m.p. −161°C).

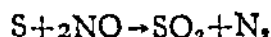
(*b*) **Chemical.** (*i*) It is neutral towards litmus.

(*ii*) **Decomposition.** It is one of the most stable oxides of nitrogen. On heating decomposition begins at 500°C and is still slight at 900°C.



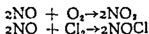
$$2NO \rightleftharpoons N_2 + O_2$$

[illegible] is incombustible and [illegible] sulphur and vigorously [illegible] feebly burning phosphorus are extinguished. Red hot iron wire burns in nitric oxide.



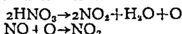
$$S + 2NO \rightarrow SO_2 + N_2$$

[illegible] ctly with oxy- [illegible] With chlorine [illegible]

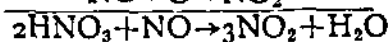


$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO + Cl_2 \rightarrow 2NOCl$$

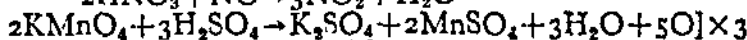
On account of this ready oxidation, it acts as a reducing agent. It reduces nitric acid and acidified potassium permanganate. In the latter case it is oxidised to nitric acid.



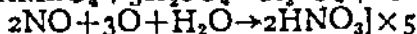
$$2HNO_3 \rightarrow 2NO_2 + H_2O + O$$
$$NO + O \rightarrow NO_2$$



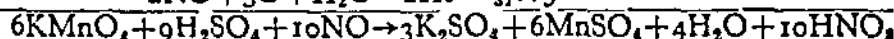
$$2HNO_3 + NO \rightarrow 3NO_2 + H_2O$$



$$[2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O] \times 3$$

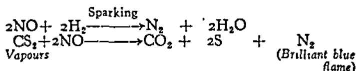


$$[2NO + 3O + H_2O \rightarrow 2HNO_3] \times 5$$

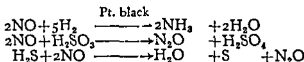


$$6KMnO_4 + 9H_2SO_4 + 10NO \rightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$$

(*v*) **Oxidising Properties.** Whenever nitric oxide is acting as an oxidising agent it is usually reduced to nitrogen but occasionally ammonia or nitrous oxide are also formed.



$$2NO + 2H_2 \xrightarrow{\text{Sparking}} N_2 + 2H_2O$$
$$\underset{\text{Vapours}}{CS_2} + 2NO \longrightarrow CO_2 + 2S + \underset{\text{(Brilliant blue flame)}}{N_2}$$



$$2NO + 5H_2 \xrightarrow{\text{Pt. black}} 2NH_3 + 2H_2O$$
$$2NO + H_2SO_3 \longrightarrow N_2O + H_2SO_4$$
$$H_2S + 2NO \longrightarrow H_2O + S + N_2O$$

(*vi*) **With Ferrous Sulphate.** It combines with ferrous sulphate to give ($FeSO_4.NO$) a dark coloured substance.

12. **Uses.**—(*i*) In the manufacture of nitric acid.

(*ii*) In the detection of oxygen to distinguish it from nitrous oxide.

(*iii*) As a catalyst in the Lead Chamber Process for the manufacture of sulphuric acid.

13. **Tests.**—(*i*) Colourless, (*ii*) Gives brown fumes with air.

14. **Formula.**—The formula of nitric oxide is determined by means of the apparatus shown in Fig. 42·4. An iron wire, which can be electrically heated, is suspended in a wide glass tube communicating with a mercury reservoir with the help of a rubber tube.

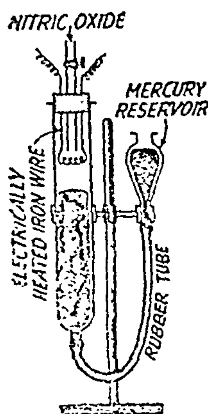


Fig. 42·4—Determination of the formula of nitric oxide.

Mercury level is raised in the wide glass tube to expel all air by raising the reservoir. Some nitric oxide is now admitted into the tube and its volume noted after equalising the mercury level in the two limbs.

Iron wire is then strongly heated electrically and nitric oxide is thereby reduced to nitrogen which after cooling is found to occupy half the volume of nitric oxide enclosed. This shows that one volume of nitric oxide contains half a volume of nitrogen.

Applying Avogadro's law to this, we conclude that one molecule of nitric oxide contains half a molecule (=1 atom) of nitrogen, *i.e.*, its formula is NO_x where x is still to be found.

From vapour density determination, the molecular weight is found to be 30. Hence

$$14+16x=30 \qquad \text{whence } x=1.$$

Hence formula of nitric oxide is NO.

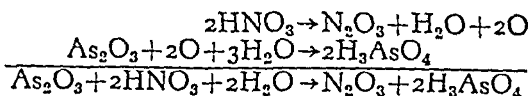
NITROGEN TRIOXIDE, N_2O_3

15. **Preparation.**—(*i*) By passing a mixture of nitric oxide and nitrogen dioxide (1 : 1) through a tube cooled below —20°C nitrogen trioxide is obtained as a blue liquid.



$$NO+NO_2 \rightarrow N_2O_3$$

(*ii*) By distilling a mixture of 60% nitric acid with arsenious oxide and condensing the vapours in a U-tube dipped in freezing mixture.



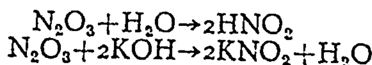
$$2HNO_3 \rightarrow N_2O_3+H_2O+2O$$
$$As_2O_3+2O+3H_2O \rightarrow 2H_3AsO_4$$
$$\overline{As_2O_3+2HNO_3+2H_2O \rightarrow N_2O_3+2H_3AsO_4}$$

16. **Properties.**—It is a blue liquid stable only below —20°C. Above this temperature it decomposes into nitric oxide and nitrogen dioxide and behaves as a mixture of these.



$$N_2O_3 \rightarrow NO+NO_2$$

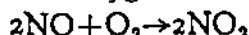
Theoretically it is the anhydride of nitrous acid and with alkalis gives nitrites.



$$N_2O_3+H_2O \rightarrow 2HNO_2$$
$$N_2O_3+2KOH \rightarrow 2KNO_2+H_2O$$

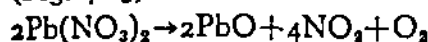
NITROGEN DIOXIDE, NO_2

17. **Preparation.**—(*i*) Nitrogen dioxide is formed when nitric oxide reacts with oxygen.



$$2NO+O_2 \rightarrow 2NO_2$$

(*ii*) **Laboratory Method.** It can be conveniently prepared in the laboratory by heating lead nitrate in a hard glass test tube (Fig. 42·5).



$$2Pb(NO_3)_2 \rightarrow 2PbO+4NO_2+O_2$$

Nitrogen dioxide is condensed to liquid nitrogen tetroxide in a U-tube dipped in a freezing mixture.

(*iii*) An alternative method for its preparation in the laboratory is by the action of concentrated nitric acid on copper chips.

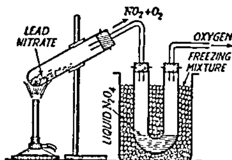
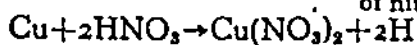
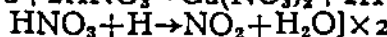


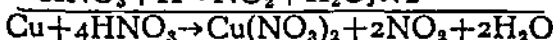
Fig. 42·5—Laboratory preparation of nitrogen dioxide.



$$Cu+2HNO_3 \rightarrow Cu(NO_3)_2+2H$$



$$[HNO_3+H \rightarrow NO_2+H_2O] \times 2$$

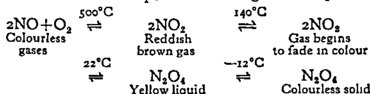


$$Cu+4HNO_3 \rightarrow Cu(NO_3)_2+2NO_2+2H_2O$$

18. **Properties of Nitrogen Dioxide.**

(*a*) **Physical.** (*i*) It is a reddish brown gas with a pungent smell.

(*ii*) It associates or decomposes with changes in temperature.



$$\underset{\text{Colourless gases}}{2NO+O_2} \overset{500°C}{\rightleftharpoons} \underset{\text{Reddish brown gas}}{2NO_2} \overset{140°C}{\rightleftharpoons} \underset{\text{Gas begins to fade in colour}}{2NO_2}$$

$$\overset{22°C}{\rightleftharpoons} \underset{\text{Yellow liquid}}{N_2O_4} \overset{-12°C}{\rightleftharpoons} \underset{\text{Colourless solid}}{N_2O_4}$$

This shows that with fall in temperature nitrogen dioxide molecules associate to give nitrogen tetroxide (N_2O_4).

(*iii*) It is soluble in water with which it further reacts chemically. It dissolves in nitric acid giving fuming nitric acid.

(*iv*) It is highly poisonous and corrodes the skin. When inhaled, it produces headache and sickness too.

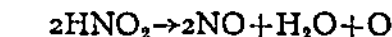
(*b*) **Chemical.** (*i*) **Acidic Nature.** Nitrogen dioxide is the mixed anhydride of nitrous and nitric acids and is thus acidic to-



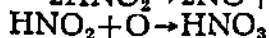
$$\ldots +HNO_3$$

$$\ldots +NaNO_3+H_2O$$

With warm water, it gives only nitric acid by auto-oxidation of nitrous acid.



$$2HNO_2 \rightarrow 2NO+H_2O+O$$



$$HNO_2+O \rightarrow HNO_3$$

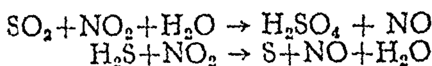


$$3HNO_2 \rightarrow HNO_3+2NO+H_2O$$

(*ii*) **Supporter of Combustion.** It is incombustible but supports the combustion of brightly burning phosphorus or magnesium ribbon. Burning sulphur or candle is, however, extinguished.

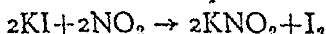
(*iii*) **Oxidising Properties.** Due to its tendency to lose nascent oxygen ($NO_2 \rightarrow NO+O$), nitrogen dioxide acts as a strong oxidising agent. For example,

(*a*) It oxidises sulphur dioxide to sulphuric acid, hydrogen sulphide to sulphur.



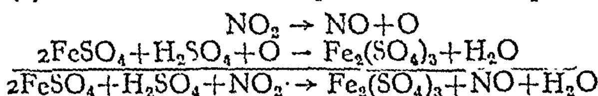
$$SO_2+NO_2+H_2O \rightarrow H_2SO_4 + NO$$
$$H_2S+NO_2 \rightarrow S+NO+H_2O$$

(*b*) It liberates iodine from potassium iodide solution.



$$2KI+2NO_2 \rightarrow 2KNO_2+I_2$$

(*c*) It oxidises ferrous sulphate to ferric sulphate.



$$NO_2 \rightarrow NO+O$$
$$2FeSO_4+H_2SO_4+O \rightarrow Fe_2(SO_4)_3+H_2O$$
$$2FeSO_4+H_2SO_4+NO_2 \rightarrow Fe_2(SO_4)_3+NO+H_2O$$

Nitric oxide obtained reacts with more of ferrous sulphate to give dark coloured nitroso-ferrous sulphate, $FeSO_4NO$.

19. **Tests.**—(*i*) Reddish brown colour.

(*ii*) Turns ferrous sulphate solution black.

20. **Uses.**—(*i*) In the manufacture of nitric acid.

(*ii*) As a catalyst in the Lead Chamber Process for the manufacture of sulphuric acid.

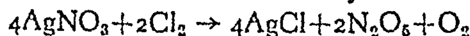
NITROGEN PENTOXIDE, N_2O_5

21. **Preparation.**—(*i*) By dehydration of concentrated nitric acid with phosphorus pentoxide.



$$4HNO_3+P_4O_{10} \rightarrow 4HPO_3+2N_2O_5$$

(*ii*) By the action of chlorine on dry silver nitrate.



$$4AgNO_3+2Cl_2 \rightarrow 4AgCl+2N_2O_5+O_2$$

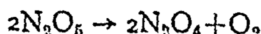
(*iii*) By passing ozone through liquid nitrogen tetroxide.



$$N_2O_4+O_3 \rightarrow N_2O_5+O_2$$

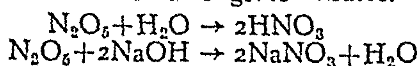
22. **Properties.**—(*i*) It is a white solid (m.p. 30°C) which readily sublimes.

(*ii*) It decomposes above its melting point and explodes when heated rapidly.



$$2N_2O_5 \rightarrow 2N_2O_4+O_2$$

(*iii*) It is the anhydride of nitric acid and reacts with water to give this acid. With alkalis it gives nitrates.



$$N_2O_5+H_2O \rightarrow 2HNO_3$$
$$N_2O_5+2NaOH \rightarrow 2NaNO_3+H_2O$$

(*iv*) Due to its easy decomposition, it acts as a powerful oxidising agent. It destroys all organic substances.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Sodium nitrate+Ammonium sulphate.

2. Nitric acid+(i) Stannous chloride+*Hydrochloric acid*, (*ii*) Arsenious oxide, (*iii*) Phosphorus pentoxide.

3. Nitrous oxide+(*i*) Carbon, (*ii*) Sulphur, (*iii*) Phosphorus, (*iv*) Copper.

4. Copper+(*i*) Dilute nitric acid, (*ii*) Concentrated nitric acid.

5. Potassium nitrate+Ferrous sulphate+Sulphuric acid.

6. Nitric oxide+(*i*) Sulphur, (*ii*) Oxygen, (*iii*) Chlorine, (*iv*) Nitric acid, (*v*) Acidified potassium permanganate, (*vi*) Hydrogen, (*vii*) Sulphurous acid, (*viii*) Ferrous sulphate.

7. Nitrogen trioxide+(*i*) Water, (*ii*) Caustic potash, (*iii*) Heated.

8. Action of heat on (*i*) Lead nitrate, (*ii*) Calcium nitrate, (*iii*) Sodium nitrate, (*iv*) Ammonium nitrate.

9. Nitrogen dioxide+(*i*) Water, (*ii*) Caustic alkali, (*iii*) Sulphur dioxide, (*iv*) Potassium iodide, (*v*) Ferrous sulphate.

10. Silver nitrate+Chlorine.

11. *Nitrogen tetroxide*+Ozone.

12. Nitrogen pentoxide+(*i*) Water, (*ii*) Sodium hydroxide, (*iii*) Heated.

QUESTIONS

Essay-type Questions

1. Describe with a neat sketch the laboratory preparation of nitrous and nitric oxides. Give their important properties and uses.

2. Name the oxides of nitrogen and give their formulae. Which of these oxides give rise to acids ? Select three of the oxides and show how they can be prepared from nitric acid. (*Bihar H S. 1961 Supp*)

3. Describe the properties and uses of nitrous oxide. How would you (*i*) distinguish it from oxygen, and (*ii*) establish its composition ? (*Bihar H.S. 1965, 62*)

4. Enumerate the various method … sised and describe in detail the laboratory … the important properties and uses of … *identified ?* (*Delhi H.S. 1970*)

5. (*a*) Write a short note on laughing gas.

(*b*) How are the oxides and nitrogen prepared ? Give their properties.

6. How are nitric oxide and nitrogen dioxide prepared ? Name three other oxides of nitrogen and write their formulae.

7. Give the names and formulae of oxides of nitrogen. How will you distinguish one from the other ?

Test Your Understanding

8. Fill in the blanks :

… water.

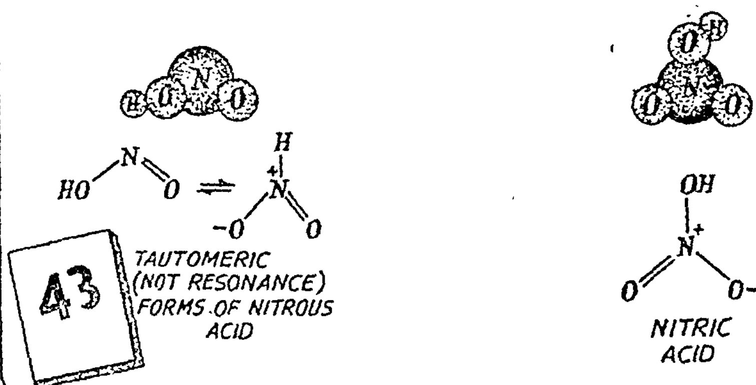
… en dioxide

behaves as … agent.

(

KEY

(*a*) N_2O, NO, N_2O_3, NO_2 and N_2O_5 ; (*b*) N_2O, hot ; (*c*) nitrogen trioxide ; (*d*) N_2O_4 ; (*e*) nitrogen dioxide and oxygen are ; (*f*) N_2O ; (*g*) a dark colour due to formation of $FeSO_4.NO$ is obtained.



Oxy-Acids of Nitrogen

NITROUS ACID, HNO_2

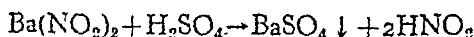
1. **Introduction.**—Nitrous acid is one of the most unstable acids and has never been isolated in a pure state. Its presence and composition have been inferred from the properties and composition of its salts.

2. **Preparation.**—(*i*) By addition of water to its anhydride, N_2O_3 (or a mixture of $NO+NO_2$ at low temperature).



$$N_2O_3+H_2O \rightarrow 2HNO_2$$

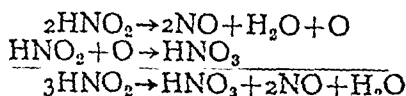
(*ii*) By adding ice-cold sulphuric acid (calculated quantity) to a well-cooled solution of barium nitrite.



$$Ba(NO_2)_2+H_2SO_4 \rightarrow BaSO_4\downarrow+2HNO_2$$

3. **Properties.**—(i) It has a slight bluish colour in solution. This may be due to the anhydride, N_2O_3 and not the acid.

(*ii*) **Decomposition.** It is very unstable. Even in the cold, it undergoes auto-oxidation (simultaneous oxidation and reduction) on standing.



$$2HNO_2 \rightarrow 2NO+H_2O+O$$
$$HNO_2+O \rightarrow HNO_3$$
$$3HNO_2 \rightarrow HNO_3+2NO+H_2O$$

At higher temperatures it decomposes into nitric oxide and nitrogen dioxide.



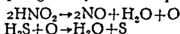
$$2HNO_2 \rightarrow NO+NO_2+H_2O$$

(*iii*) **Oxidising properties.** Due to the ease with which it can decompose to give nascent oxygen it acts as an oxidising agent.

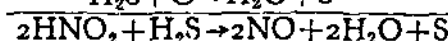


$$2HNO_2 \rightarrow 2NO + H_2O + O$$

It oxidises—(*a*) *Hydrogen sulphide to Sulphur* :

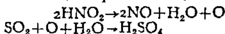


$$2HNO_2 \rightarrow 2NO + H_2O + O$$
$$H_2S + O \rightarrow H_2O + S$$

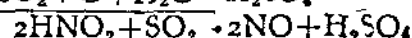


$$2HNO_2 + H_2S \rightarrow 2NO + 2H_2O + S$$

(*b*) *Sulphur dioxide to sulphuric acid* :

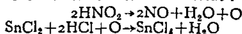


$$2HNO_2 \rightarrow 2NO + H_2O + O$$
$$SO_2 + O + H_2O \rightarrow H_2SO_4$$

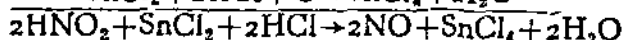


$$2HNO_2 + SO_2 \rightarrow 2NO + H_2SO_4$$

(*c*) *Stannous chloride to Stannic chloride* :

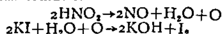


$$2HNO_2 \rightarrow 2NO + H_2O + O$$
$$SnCl_2 + 2HCl + O \rightarrow SnCl_4 + H_2O$$

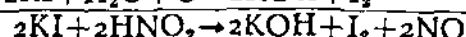


$$2HNO_2 + SnCl_2 + 2HCl \rightarrow 2NO + SnCl_4 + 2H_2O$$

(*d*) *Potassium iodide to Iodine* :

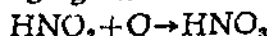


$$2HNO_2 \rightarrow 2NO + H_2O + O$$
$$2KI + H_2O + O \rightarrow 2KOH + I_2$$



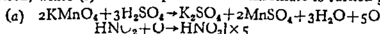
$$2KI + 2HNO_2 \rightarrow 2KOH + I_2 + 2NO$$

(*iv*) **Reducing properties.** Towards strong oxidising agents it acts as a reducing agent as it is easily oxidised to nitric acid.

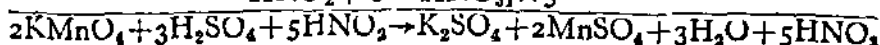


$$HNO_2 + O \rightarrow HNO_3$$

For example, (*a*) acidified potassium permanganate is decolorised, while (*b*) acidified potassium dichromate is turned green.



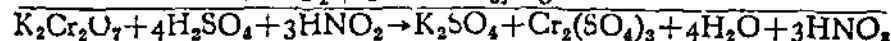
$$(a) \quad 2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$
$$HNO_2 + O \rightarrow HNO_3] \times 5$$



$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3$$

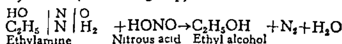


$$(b) \quad K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$
$$HNO_2 + O \rightarrow HNO_3] \times 3$$



$$K_2Cr_2O_7 + 4H_2SO_4 + 3HNO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3HNO_3$$

(*v*) **Action on Organic Compounds.** Nitrous acid reacts with organic compounds containing $—NH_2$ (amino group) and replaces the group by —OH (alcoholic group).

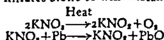


$$C_2H_5NH_2 + HONO \rightarrow C_2H_5OH + N_2 + H_2O$$

Ethylamine — Nitrous acid — Ethyl alcohol

4. **Uses.**—Nitrous acid is used in the manufacture of azo-dyes. It is prepared there by the action of ice-cold dilute acid on sodium nitrite.

5. Nitrites.—The salts of nitrous acid are called nitrites and are quite stable. Like the acid, nitrites are also prepared by special methods, *e.g.*, reduction of the corresponding nitrates alone or with metallic lead.

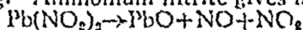


$$2KNO_3 \xrightarrow{Heat} 2KNO_2 + O_2$$
$$KNO_3 + Pb \longrightarrow KNO_2 + PbO$$

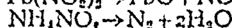
Nitrites in the soil are formed as a result of bacterial action on orga nitrogenous matter of animal or plant origin. Presence of nitrites in drink water indicates that it is contaminated.

Tests for nitrites. (i) Nitrites of Alkali metals are yellow crystall solids. All nitrites are soluble in water except silver nitrite which is soluble hot water.

(ii) *Action of heat.* All nitrites except those of alkali metals give oxides of nitrogen on heating. Ammonium nitrite gives nitrogen.

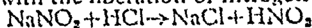


$$Pb(NO_2)_2 \rightarrow PbO + NO + NO_2$$

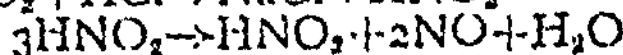


$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

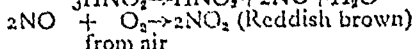
(iii) *Action of dilute acids.* With dilute sulphuric or hydrochloric a nitrites are decomposed with the liberation of nitrogen dioxide.



$$NaNO_2 + HCl \rightarrow NaCl + HNO_2$$



$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$



$$\underset{}{2NO} + \underset{\text{from air}}{O_2} \rightarrow 2NO_2 \text{ (Reddish brown)}$$

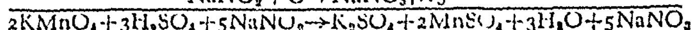
(iv) *Reducing property.* Nitrites decolorize acidified potassium perm ganate solution.



$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$



$$[NaNO_2 + O \rightarrow NaNO_3] \times 5$$



$$2KMnO_4 + 3H_2SO_4 + 5NaNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5NaNO_3$$

(v) *With ferrous sulphate solution.* A nitrite solution when added to acidified solution of ferrous sulphate, colours it black due to the formation $FeSO_4.NO$.

(vi) From an acidified solution of potassium iodide, nitrites liber iodine.

(vii) With meta-phenylenediamine solution in hydrochloric acid, nitri give a brown colour.

NITRIC ACID, HNO_3

6. Historical and Occurrence.—Nitric acid was called *aqua fo* (=strong water) by alchemists. Glauber (1650) prepared it from nitre and s phuric acid but it was left for Lavoisier (1776) to prove that it contained oxyg Cavendish (1784-85) stated that nitric acid could be formed by passing elec sparks through a mixture of nitrogen and moist oxygen. Traces of ni acid occur in air where it is formed by electric discharges and is washed do by rain.

7. Preparation of Nitric Acid in the Laboratory.

—Nit acid is prepared in the laboratory by heating a nitrate (sodiu nitrate or potassiu nitrate) and concer rated sulphuric ac in a retort (Fig. 43·



$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HN($$

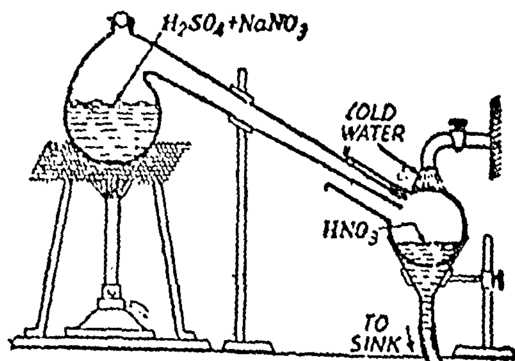
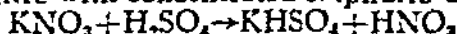


Fig. 43·1—Preparation of nitric acid in the laboratory.

Vapours of ni ric acid are conden ed to a brown liqu in a receiver cool under cold wate Dissolved oxides nitrogen are remo ed by redistillatio or by blowing current of carbon dioxide or dry air through the warm acid.

8. Manufacture of Nitric Acid.—(*i*) From Nitre. Before the Great War the only method for the manufacture of nitric acid was by distilling nitre with concentrated sulphuric acid.



$$KNO_3+H_2SO_4 \rightarrow KHSO_4+HNO_3$$

The mixture is placed in a cast iron retort (Fig. 43·2) and distilled. The vapours are condensed by passing through silica

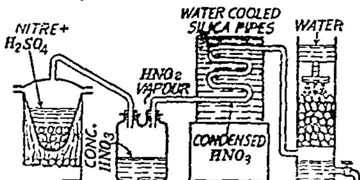
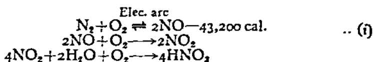


Fig. 43·2—Manufacture of nitric acid from nitre.

condensers when condensed acid flows into the receiver. Any uncondensed vapours pass up another tower down which cold water is sprayed. Dilute nitric acid produced is collected in another receiver.

(*ii*) From Air (Birkland and Eyde Process)

Theory. The process is based on the following chemical reactions :



$$N_2+O_2 \overset{\text{Elec. arc}}{\rightleftharpoons} 2NO-43{,}200 \text{ cal.} \quad \text{.. (i)}$$
$$2NO+O_2 \longrightarrow 2NO_2$$
$$4NO_2+2H_2O+O_2 \longrightarrow 4HNO_3$$

The reaction (*i*) being reversible and endothermic is favoured by high temperature according to Le Chatelier's principle.

Process Air is blown into an electric arc struck between two water-cooled copper electrodes and spread into a disc with the help of a magnetic field at right angles (Fig. 43·3). The issuing gases containing about 1·25 per cent nitric oxide are cooled down

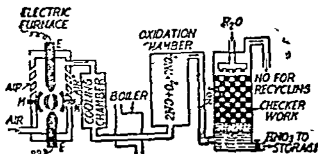


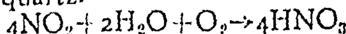
Fig. 43·3—Birkland and Eyde Process for the manufacture of nitric acid from air.

quickly to 1000°C to arrest the backward reaction (decomposition of nitric oxide). This is cooled further to about 150°C by passing through boiler pipes and the heat used for steam raising. The gases next pass through oxidation chamber where nitric oxide is oxidised to nitrogen dioxide.



$$2NO + O_2 \rightarrow 2NO_2$$

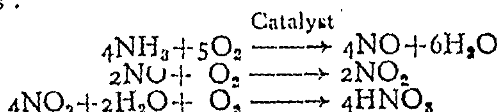
Nitrogen dioxide produced is absorbed in water in the presence of excess of air to give nitric acid* in the absorption tower packed with quartz.



$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

(*iii*) **From Ammonia (Ostwald's Process).** Large quantities of ammonia manufactured by Haber's Process are converted into nitric acid by Ostwald's Process.

Theory. The process is based on the following chemical reactions :



$$4NH_3 + 5O_2 \xrightarrow{\text{Catalyst}} 4NO + 6H_2O$$
$$2NO + O_2 \longrightarrow 2NO_2$$
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Process. A mixture of ammonia gas with air in the ratio 1 : 8 is passed through a catalyst chamber containing platinum

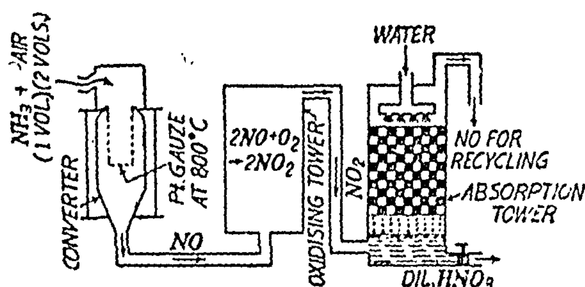
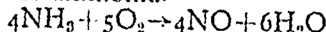


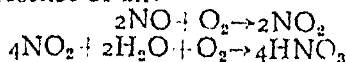
Fig. 43·4 Ostwald's Process for the manufacture of nitric acid.

gauze heated to 800°C (Fig. 43·4). Here nitric oxide is produced by catalytic oxidation of ammonia.



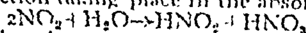
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The gases next pass through the *oxidising tower* where nitric oxide is oxidised to nitrogen dioxide which passes up the absorption tower packed with earthen balls when a stream of water flows down. Nitric acid is produced by absorption of nitrogen dioxide in water in presence of air.



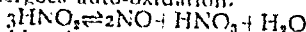
$$2NO + O_2 \rightarrow 2NO_2$$
$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

*The principal reaction taking place in the absorption tower is



$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

Nitric acid formed undergoes auto-oxidation.



$$3HNO_2 \rightleftharpoons 2NO + HNO_3 + H_2O$$

Nitric oxide is reoxidised by air present to nitrogen dioxide which is absorbed again as shown above



$$2NO + O_2 \rightarrow 2NO_2$$

Dilute nitric acid obtained may be concentrated by distillation under reduced pressure in presence of concentrated sulphuric acid or used as such in the manufacture of basic calcium nitrate (a manure) by dissolving limestone in the dilute nitric acid.

9. Properties of Nitric Acid.

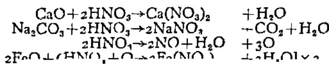
(*a*) Physical. (*i*) It is a colourless fuming liquid when pure, but may be coloured yellow by its dissociation products mainly nitrogen dioxide. Nitric acid containing dissolved nitrogen dioxide is called *fuming nitric acid*.

(*ii*) It has an extremely corrosive action on the skin and causes painful sores.

(*iii*) It forms a constant boiling mixture with water, boiling at 121°C and containing 68 per cent of the acid. Dilute acid cannot, therefore, be concentrated beyond 68 per cent by boiling. This is the concentrated acid sold in the market.

(*iv*) Pure acid has a specific gravity of 1·54. It boils at 86°C and freezes to a white solid (m.p. −42°C).

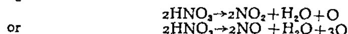
(*b*) Chemical. (1) Nitric acid as an acid. Is a very strong acid and exhibits the usual properties of acids. Thus it reacts with basic oxides, hydroxides, and carbonates forming corresponding salts. In case the metallic radical is a reducing agent, *e.g.*, in ferrous oxide, it is oxidised in addition to the salt formation.



$$CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$$
$$Na_2CO_3 + 2HNO_3 \rightarrow 2NaNO_3 + CO_2 + H_2O$$
$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$
[illegible]

or

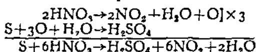
(2) As an oxidising agent. Due to the ease with which it decomposes to give nascent oxygen, it acts as a powerful oxidising agent.



$$2HNO_3 \rightarrow 2NO_2 + H_2O + O$$
or
$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$

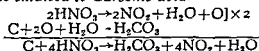
(*a*) Action on non-metals The nascent oxygen oxidises the various non-metals to their corresponding highest oxy-acids. For example :

(*i*) *Sulphur is oxidised to Sulphuric acid.*



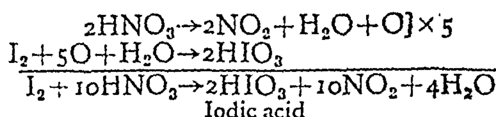
$$2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 3$$
$$S + 3O + H_2O \rightarrow H_2SO_4$$
$$S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$$

(*ii*) *Carbon is oxidised to Carbonic acid.*



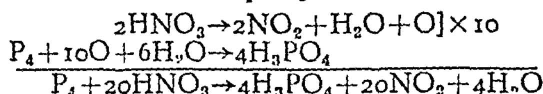
$$2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 2$$
$$C + 2O + H_2O \rightarrow H_2CO_3$$
$$C + 4HNO_3 \rightarrow H_2CO_3 + 4NO_2 + H_2O$$

(*iii*) *Iodine is oxidised to Iodic acid.*



$$2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 5$$
$$I_2 + 5O + H_2O \rightarrow 2HIO_3$$
$$I_2 + 10HNO_3 \rightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10NO_2 + 4H_2O$$

(*iv*) *Phosphorus is oxidised to phosphoric acid.*

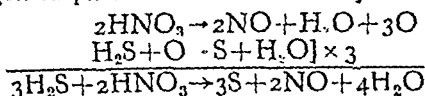


$$2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 10$$
$$P_4 + 10O + 6H_2O \rightarrow 4H_3PO_4$$
$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Similarly arsenic is oxidised to arsenic acid (H_3AsO_4), antimony to antimonic acid (H_3SbO_4) and tin to metastannic acid (H_2SnO_3).

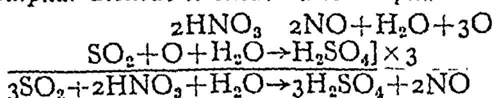
(*b*) **Action on compounds.** It oxidises a large number of compounds also. For example :

(*i*) *Hydrogen sulphide is oxidised to Sulphur.*



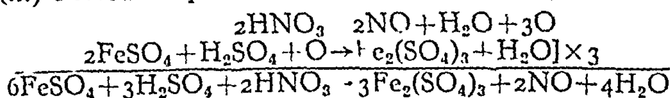
$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$
$$H_2S + O \rightarrow S + H_2O] \times 3$$
$$3H_2S + 2HNO_3 \rightarrow 3S + 2NO + 4H_2O$$

(*ii*) *Sulphur dioxide is oxidised to Sulphuric acid.*



$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$
$$SO_2 + O + H_2O \rightarrow H_2SO_4] \times 3$$
$$3SO_2 + 2HNO_3 + H_2O \rightarrow 3H_2SO_4 + 2NO$$

(*iii*) *Ferrous sulphate is oxidised to Ferric sulphate.*



$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$
$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$
$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

The nitric oxide formed gives a dark brown ring of nitroso ferrous sulphate, $FeSO_4 \cdot NO$, with more of ferrous sulphate present.

(3) **Action on metals.** In its action on metals, nitric acid acts both as an acid and an oxidising agent. The metals are oxidised to their corresponding positive ions whereas nitric acid is reduced to NO_2, NO, N_2O, N_2 or NH_4^+ depending upon :

(*i*) the nature of the metals,

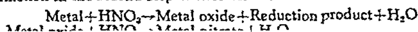
(*ii*) concentration of the acid, and

(*iii*) temperature.

In the case of metals of variable valency like mercury, tin and iron, dilute acid with excess of the metal yields *-ous* salt (mercurous, ferrous, etc.) while excess of concentrated acid yields *-ic* salt.

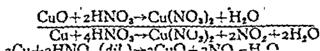
(*a*) **The less active metals**, *e.g.*, copper, silver, lead and mercury, reduce concentrated nitric acid to nitrogen dioxide while with dilute acid nitric oxide is formed.

The precise mechanism of these reactions is still obscure. These metals do not give hydrogen with dilute acids. It is, therefore, believed that in the first step metals are oxidised (with the consequent reduction of nitric acid). This is followed by salt formation in the second step as illustrated below :



$$\text{Metal}+HNO_3\rightarrow\text{Metal oxide}+\text{Reduction product}+H_2O$$

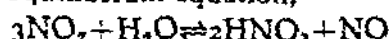
$$\text{Metal oxide}+HNO_3\rightarrow\text{Metal nitrate}+H_2O$$



$$CuO+2HNO_3\rightarrow Cu(NO_3)_2+H_2O$$

$$Cu+4HNO_3\rightarrow Cu(NO_3)_2+2NO_2+2H_2O$$

In most cases both nitrogen dioxide and nitric oxide are produced. From the equilibrium equation,

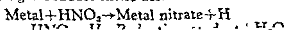


$$3NO_2+H_2O\rightleftharpoons 2HNO_3+NO$$

we learn that concentrated acid favours evolution of nitrogen dioxide.

(*b*) The more active metals, *e.g.*, zinc, iron and tin, reduce dilute nitric acid to nitrous oxide (N_2O) while very dilute nitric acid is reduced to ammonium nitrate.

These metals react with dilute acids and liberate hydrogen. It is, therefore, believed that in the first step metal reacts with nitric acid to give metal nitrate and nascent hydrogen. In the second step nascent hydrogen reduces nitric acid.

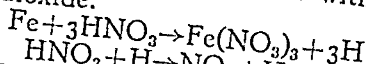


$$\text{Metal}+HNO_3\rightarrow\text{Metal nitrate}+H$$

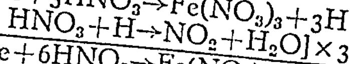
Adding :

Concentrated nitric acid with zinc gives zinc nitrate+nitrogen dioxide.

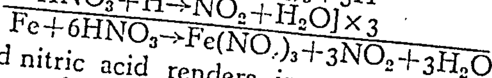
Moderately concentrated nitric acid with iron gives ferric nitrate+nitrogen dioxide.



$$Fe+3HNO_3 \rightarrow Fe(NO_3)_3+3H$$



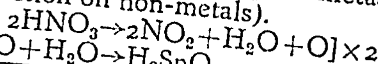
$$HNO_3+H \rightarrow NO_2+H_2O] \times 3$$



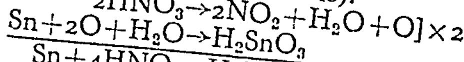
$$Fe+6HNO_3 \rightarrow Fe(NO_3)_3+3NO_2+3H_2O$$

Concentrated nitric acid renders iron passive. Nickel and chromium are also rendered passive similarly.

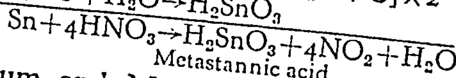
Tin with concentrated nitric acid gives metastannic acid+nitrogen dioxide (*cf.*, Action on non-metals).



$$2HNO_3 \rightarrow 2NO_2+H_2O+O] \times 2$$

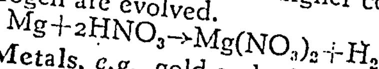


$$Sn+2O+H_2O \rightarrow H_2SnO_3$$



$$Sn+4HNO_3 \rightarrow \underset{\text{Metastannic acid}}{H_2SnO_3}+4NO_2+H_2O$$

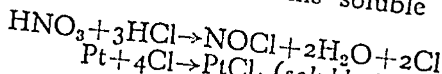
(*c*) **Magnesium and Manganese** react with very dilute nitric acid to liberate hydrogen. With higher concentration of the acid oxides of nitrogen are evolved.



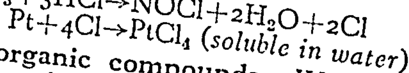
$$Mg+2HNO_3 \rightarrow Mg(NO_3)_2+H_2$$

(*d*) **Noble Metals,** *e.g.*, gold and platinum do not react with nitric acid. With aluminium the reaction is so very slow that we usually say nitric acid has "no action on aluminium".

Noble metals are, however, dissolved by *aqua regia*, a mixture of one part of nitric acid with three parts of hydrochloric acid. It liberates nascent chlorine which forms soluble chlorides with noble metals.



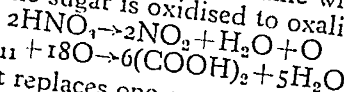
$$HNO_3+3HCl \rightarrow NOCl+2H_2O+2Cl$$



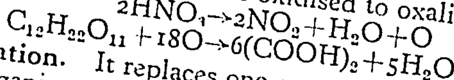
$$Pt+4Cl \rightarrow PtCl_4 \text{ (soluble in water)}$$

(4) **Action on organic compounds.** With organic compounds nitric acid brings about either *oxidation* or *nitration*.

(*a*) **Oxidation.** It oxidises organic compounds to carbon dioxide and water. Thus sawdust catches fire when nitric acid is poured on it and turpentine oil bursts into flame when poured into fuming nitric acid. Cane-sugar is oxidised to oxalic acid.

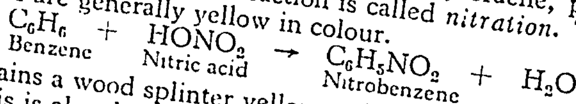


$$2HNO_3 \rightarrow 2NO_2+H_2O+O$$



$$C_{12}H_{22}O_{11}+18O \rightarrow 6(COOH)_2+5H_2O$$

(*b*) **Nitration.** It replaces one or more hydrogen atoms of an aromatic organic compound, *e.g.*, benzene, toluene, phenol, by a nitro group ($-NO_2$). The reaction is called *nitration*. The nitro-compounds are generally yellow in colour.



$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Nitric acid}}{HONO_2} \rightarrow \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$$

It stains a wood splinter yellow and gives yellow stains on the skin. This is also due to the formation of nitrocellulose with wood splinter or skin.

Products of the Action of Nitric acid on Metals (Summary)

Metals	Cu, Ag, Pb	Hg	Zn	Sn	Fe	Mg, Mn
Conc. acid	NO_2	NO_2+ -ic salt	NO_2	H_2SnO_3 $+NO_2$	NO_2*	
Dil. acid	NO	NO+ -ous salt	N_2O or NH_4NO_3	N_2O or NH_4NO_3	NH_4NO_3	Oxides of nitrogen H_2

*Very conc. HNO_3 makes iron passive.

NITRIC ACID AND ITS USES

AQUA REGIA



DYES AND DRUGS

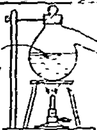


EXPLOSIVES



FERTILIZERS







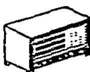
$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$



RAYON

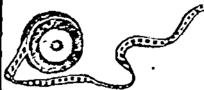


LACQUER





PLASTICS



CINEMA FILM

10. **Uses of Nitric Acid.**—It is used :

(*a*) In the manufacture of (*i*) *Fertilizers, e.g.*, Basic calcium nitrate [$CaO\ Ca(NO_3)_2$] is prepared by the action of dilute nitric acid on limestone.

(*ii*) *Explosives, e.g.*, nitroglycerine, dynamite, T.N.T., picric acid and smokeless powder.

(*iii*) *Perfumes, dyes and medicines* from coal-tar products.

(*iv*) *Artificial silk*, which is a cellulose nitrate

(*v*) *Sulphuric acid* wherein nitric acid and oxides of nitrogen are used as catalyst (in the Lead Chamber Process).

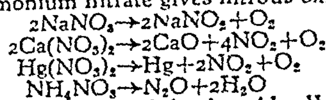
(*b*) In the purification of gold and silver.

(*c*) As an important reagent in the laboratory.

11. **Nitrates.**—Salts of nitric acid are called nitrates. Sodium and potassium nitrates occur in nature while others can be prepared by the action of nitric acid on metals, their oxides, hydroxides or carbonates.

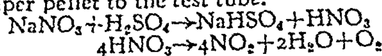
General properties. (*i*) Nitrates are generally soluble in water.

(*ii*) **Action of heat.** Alkali nitrates give nitrites and oxygen on heating, heavy metal nitrates give metal oxide and nitrogen dioxide (Mercuric nitrate gives mercury) and ammonium nitrate gives nitrous oxide.



$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$
$$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$$
$$Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$$
$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

(*iii*) **Action of concentrated sulphuric acid.** When heated with concentrated sulpuric acid, nitrates liberate nitric acid vapours partially reduced to nitrogen dioxide. Copious fumes of nitrogen dioxide are obtained on adding copper chips or paper pellet to the test tube.



$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2$$

(*iv*) These are good oxidising agents and as such are used in gun powder and explosives.

12. **Tests for Nitrates.**—(*i*) Action of heat, and (*ii*) heating with concentrated sulpuric acid is explained above.

(iii) **Ring Test.** To a nitrate solution is added ferrous sulphat solution. Precipitate, if any, is filtered off and concentrated sulphuric acid i poured along the sides. *A black ring is obtained at the junction of the tw* liquids due to the formation of $FeSO_4.NO$.

(*iv*) With diphenylamine, nitrates give a blue colour while with brucin solution a red colour is obtained.

13. **Distinguishing Tests between Nitrites and Nitrates.**

Tests	Nitrites	Nitrates
1. Heat the salt with dilute hydrochloric acid.	Brown fumes of NO_2:turns $FeSO_4$ solution dark brown.	No action.
2. *Ring test.* To the salt solution add $FeSO_4$ and H_2SO_4.	Dark brown colour even with dil. H_2SO_4.	A dark brown rir *is formed* wi concentrated H_2SO_4 only.
3. To the acidified solution of the salt add KI solution.	Iodine liberated.	No action.
4. To the salt solution add brucine solution.	No action.	Red colour.
5. To acidified salt solution add $KMnO_4$.	Decolorised.	No action.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reaction, if any, between :

1. Nitrous acid+(i) H_2S, (ii) SO_2, (iii) Acidified $SnCl_2$, (iv) KI, (v) Acidified $KMnO_4$, (vi) Acidified $K_2Cr_2O_7$, (vii) When heated, (viii) Auto-oxidation.

2. Nitre+Sulphuric acid.

3. Nitric acid+(i) CaO ; (ii) Na_2CO_3 ; (iii) FeO : (iv) Sulphur, carbon, iodine, phosphorus : (v) H_2S, SO_2 ; (vi) Copper, mercury, zinc, iron, tin, magnesium, manganese : (vii) Sugar, benzene.

4. Platinum+Aqua regia.

QUESTIONS

Essay-type Questions

1. How is nitrous acid obtained in the laboratory ? "Nitrous acid behaves sometimes as an oxidising agent and sometimes as reducing agent." Justify the statement giving examples. *(Bihar H.S. 1964)*

2. How is nitric acid prepared in the laboratory ? What are its principal chemical properties ? Name three explosives which are prepared from it. *(Punjab H.S. 1962)*

3. (a) How is nitric acid manufactured ? Give its reactions with (i) magnesium, (ii) sulphur, (iii) phosphorus. *(All India H.S. 1969)*

(b) Given only the gases N_2, O_2 and H_2, show how you could prepare each of the following compounds. Include all appropriate equations.

(i) NO_2, (ii) HNO_3, (iii) NH_3. *(Punjab Pre-Univ. 1969)*

4. Describe the preparation of nitric acid on a commercial scale. Mention some important uses of nitric acid in industry. *(M.P. Inter. 1964 ; Bihar H.S. 1966, 64 Supp, 63, 62)*

5. (a) How will you distinguish a nitrite from a nitrate ? *(Delhi Pre-Medical 1962)*

(b) What do you get on heating : (i) Ammonium nitrate, (ii) Potassium nitrate, and (iii) Mercuric nitrate ? *(Punjab Inter. 1960)*

6. Describe a process for the manufacture of nitric acid from (a) air, (b) ammonia ; give the various steps involved in the process. Mention its properties and uses.

How does strong nitric acid react with carbon, sulphur, arsenic, magnesium, copper, iron, potassium iodide and sulphur dioxide ? *(All India H.S. 1967 ; Delhi H.S. 1963 ; Punjab Pre-Univ. 1971)*

Test Your Understanding

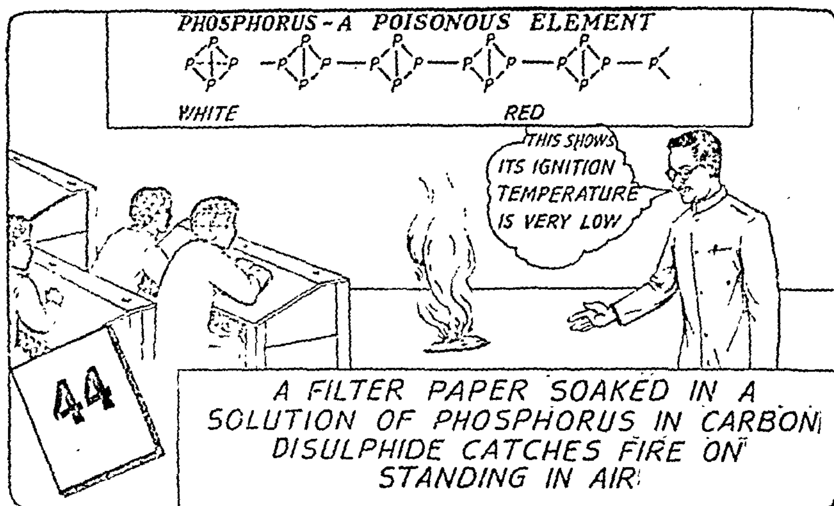
7. Comment on the following statements concerning nitric acid, illustrating your answer with suitable examples .

(a) It acts both as an oxidising and a reducing agent.

(b) It can be made by reducing ammonia.

(c) It is an acid of which N_2O is the anhydride.

(d) Though it does not react with charcoal, it readily oxidises sulphur. *(Delhi H.S. 1962*



Phosphorus

1. **Historical.**—Phosphorus was discovered in 1669 by Brand who got it by distillation of evaporated urine while looking for the Philosopher's stone. It glowed in the dark and was, therefore, called Phosphorus (meaning *Light bearing*). Boyle got it in 1681 and wasthe first to publish the method of preparation. Scheele got it from bone-ash in 1771 but its elementary nature was shown by Lavoisieinr 1777

2. **Occurrence.**—Phosphorus occurs in combination only as phosphates. For example, *Phosphorite*, $Ca_3(PO_4)_2$; *Chlorapatite*, $3Ca_3(PO_4)_2CaCl_2$; *Fluorapatite*, $3Ca_3(PO_4)_2.CaF_2$.

In addition to these, phosphorus is present in phosphoproteins of the brain, bones, teeth and nervous tissues of animals and inplants.

3. **Commercial Preparation.**—Phosphorus is manufactured from calcium phosphate by one of the two processes given below :

(*a*) **Modern Electro-Thermic Process.** Calcium phosphate needed for the manufacture phosphorus is obtained from mineral phosphorite or bones. The bones are subjected to destructive distillation when bone charcoal is obtained. Bone charcoal is then burnt to get bone-ash.

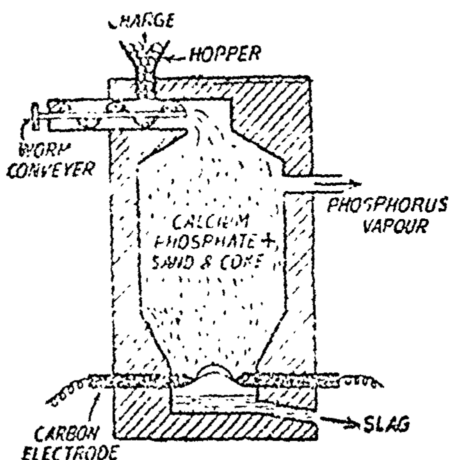
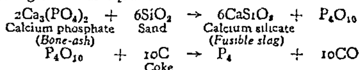


Fig. 44·1—Modern electro-thermic method for the manufacture of phosphorus.

Bone-ash is mixed with coke and sand and put into the hopper of an electric furnace (Fig. 44·1). From here it is fed into the furnace with the help of a worm conveyer. The mixture is heated to about 1000°C by striking an electric arc between two carbon electrodes. The chemi-

cal reactions taking place in the furnace may be represented by the following chemical equations :

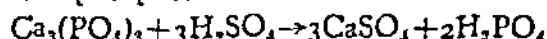


$$\underset{\substack{\text{Calcium phosphate}\\ \textit{(Bone-ash)}}}{2Ca_3(PO_4)_2} + \underset{\text{Sand}}{6SiO_2} \rightarrow \underset{\substack{\text{Calcium silicate}\\ \textit{(Fusible slag)}}}{6CaSiO_3} + P_4O_{10}$$

$$P_4O_{10} + \underset{\text{Coke}}{10C} \rightarrow P_4 + 10CO$$

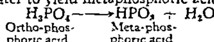
Vapours of phosphorus leave the furnace through an exit near the top and are condensed under water while calcium silicate fusible slag) is tapped from the slag hole below. Phosphorus so obtained may be purified by melting under acidified potassium dichromate and redistilling.

(b) **Old Process.** In the old process mineral phosphorite or bone-ash as obtained in the above process is heated with the requisite quantity of concentrated sulphuric acid to form insoluble calcium sulphate and ortho-phosphoric acid.



$$Ca_3(PO_4)_2+3H_2SO_4\rightarrow 3CaSO_4+2H_3PO_4$$

The syrupy acid is filtered and evaporated when ortho-phosphoric acid loses water to yield metaphosphoric acid.



$$\underset{\text{Ortho-phosphoric acid}}{H_3PO_4} \longrightarrow \underset{\text{Meta-phosphoric acid}}{HPO_3} + H_2O$$

Meta-phosphoric acid so obtained is mixed with powdered coke and distilled in fire-clay retorts (Fig. 44·2) at a bright red heat.

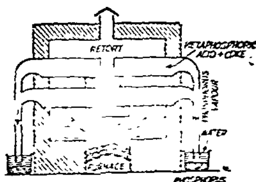
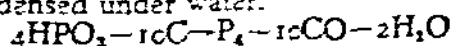


Fig. 44·2—Manufacture of phosphorus (Old Process).

The acid is reduced by coke to phosphorus which vaporizes and the vapours are condensed under water.



$$4HPO_3+10C\rightarrow P_4+10CO+2H_2O$$

Phosphorus obtained is purified as given before in the previous process.

4. Allotropic Modifications of Phosphorus.—Phosphorus is another example of elements which exhibit allotropy. Various allotropic modifications of phosphorus are :

(i) White or yellow phosphorus, (ii) Red phosphorus,

(iii) Scarlet phosphorus, (iv) Violet phosphorus, and

(v) Black phosphorus.

5. White Phosphorus.—Phosphorus manufactured by any of the two processes given above is white phosphorus.

Properties of White Phosphorus.

(*a*) **Physical.** (*i*) When freshly prepared, it is nearly colourless but acquires a pale lemon-yellow colour on standing. It is, therefore, often called yellow phosphorus.

(*ii*) It is a transparent waxy solid (Sp. Gr. 1·8 to 20°C) which can be easily cut with a knife.

(*iii*) It melts at 44°C but as its ignition temperature is very low (35°C), it can be melted only under water to prevent combustion. In the absence of air it boils at 290°C.

(*iv*) It has a characteristic garlic smell, and is poisonous in nature. Labourers working with phosphorus suffer from a disease in which the jaw bones decay (*Phossy jaw*).

(*v*) It is insoluble in water but is readily soluble in carbon disulphide and oils.

(*vi*) Its molecular weight corresponds to the molecular formula P_4.

(*b*) **Chemical.** (i) **phosphorescence.** In contact with air, it undergoes slow combustion and glows in the dark. *This property of glowing of phosphorus in the dark is called phosphorescence.*

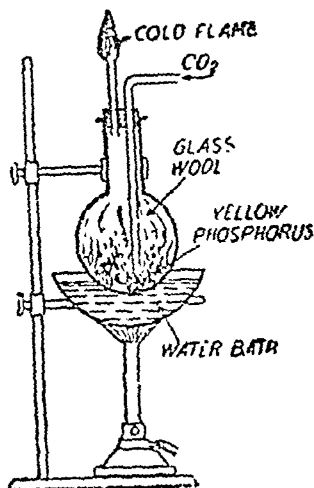
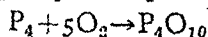


Fig. 44·3—Cold flame experiment.

Expt. 1. Place some white phosphorus and glass wool in a round-bottom flask fitted with a jet tube and a delivery tube (Fig. 44·3). Switch off the lights in the room and pass a stream of carbon dioxide in the flask as it is heated on the water bath. A flame is seen at the mouth of the jet and is found to be cold to touch. Carbon dioxide is sweeping out vapours of phosphorus which escape through the jet and glow in the dark (*Cold flame experiment*).

(*ii*) **Burning.** Its ignition temperature being very low, it readily catches fire in air giving dense white fumes of phosphorus pentoxide.

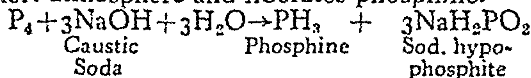


$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

CAUTION : *White phosphorus must always be handled and stored under water. It should never be touched with fingers. It is a strong poison if taken internally.*

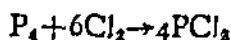
Expt. 2. Dissolve some white phosphorus in carbon disulphide, dip a filter paper in it and put it on the floor. In a few seconds carbon disulphide evaporates and filter paper, with fine particles of phosphorus on it, catces fire.

(*iii*) **With Caustic Soda.** It dissolves in caustic soda on boiling in an inert atmosphere and liberates phosphine.



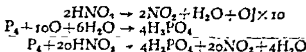
$$\underset{\text{Caustic Soda}}{P_4 + 3NaOH} + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3} + \underset{\text{Sod. hypophosphite}}{3NaH_2PO_2}$$

(*iv*) **With Halogens and Metals.** White phosphorus directly combines with halogens and a number of metals (*e.g.*, sodium, magnesium, iron, etc.) to give halides and phosphides. For example, with sodium it combines with a flash of light, on gentle heating to give sodium phosphide, Na_3P. With chlorine it gives phosphorus trichloride.



$$P_4+6Cl_2 \rightarrow 4PCl_3$$

(*v*) **Reducing Properties.** It is a powerful reducing agent. Concentrated nitric acid or sulphuric acid is reduced on heating with phosphorus. Phosphorus is oxidised to phosphoric acid in each case.



$$[2HNO_3 \rightarrow 2NO_2+H_2O+O] \times 10$$
$$P_4+10O+6H_2O \rightarrow 4H_3PO_4$$
$$P_4+20HNO_3 \rightarrow 4H_3PO_4+20NO_2+4H_2O$$

(*vi*) **Conversion to Red variety.** When heated in the absence of air and light to a temperature of 256°C, white phosphorus changes to the red variety.

(*vii*) **With Oxidising agents.** With oxidising agents like potassium chlorate or potassium nitrate, it forms explosive mixtures.

6. **Red Phosphorus.**

Manufacture. Red phosphorus is prepared by carefully heating yellow variety in an inert atmosphere for several days (about eight). Yellow phosphrous is taken in an egg-shape cast iron vessel (Fig. 44·4) provided with two jackets for thermometers T, T, an upright pipe with a safety valve and feeder at the top. *Air inside is replaced by an inert* gas (carbon dioxide or coal gas) and the vessel heated. Care is taken that the temperature does not rise above 250°C. Pressure is not allowed to rise very high by the safety valve. A trace of iodine accelerates the transformation of white *into red variety and it takes place rapidly at* much lower temperature.

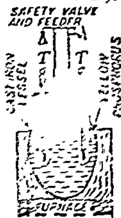


Fig. 44·4—Preparation of red phosphorus.

Red phosphorus obtained as a hard mass is powdered and boiled with caustic soda solution to remove any yellow variety still present. Red phosphorus left undissolved is thoroughly washed with water and dried.

Properties of Red Phosphorus.

(*c*) **Physical.** (*i*) *It is a dark red powder with specific gravity* 2·1.

(*ii*) It is odourless and is not poisonous.

(*iii*) It is insoluble in water as well as carbon disulphide.

(*iv*) It sublimes when heated out of contact with air to a temperature of about 290°C. Its ignition temperature is 260°C.

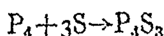
(*b*) **Chemical.** Chemically red phosphorus is much less active than the white variety. It is the stable variety of phosphorus at ordinary temperature.

(*i*) It does not glow in the dark.

(*ii*) It does not catch fire at ordinary temperature (its ignition temperature being as high as 260°C). It burns to give phosphorus pentoxide *when heated to 290°C or above.*

(*iii*) It does not react with caustic soda.

(*iv*) It combines with halogens, sulphur and metals only when heated.



$$P_4 + 3S \rightarrow P_4S_3$$

(*v*) It is converted into white variety when boiled in an inert atmosphere and the vapours condensed under water.

7. Main Points of Difference between the White and Red Varieties of Phosphorus.

Property	White Phosphorus	Red Phosphorus
1. State	Pale yellow, soft, solid, can be cut with knife. White when freshly cut.	Dark red brittle powder.
2. Odour	Garlic	Odourless.
3. Density	1·8	2·1
4. Ignition temperature	30°C (melts under water at 44°C).	260°C (does not melt but sublimes).
5. Solubility	Soluble in CS_2.	Insoluble.
6. In air	Oxidised and emits light in the dark (Phosphorescence).	Emits no light.
7. With chlorine	Combines readily gives PCl_3 and PCl_5.	Combines only on heating.
8. With hot caustic soda.	Dissolves; PH_3 liberated.	No action.
9. Physiological action.	Poisonous.	Non-poisonous.

8. **Scarlet Phosphorus.**—If a solution of red phosphorus in phosphorus *tribromide* is exposed to light or boiled, a mixture of red phosphorus and the solvent separates as scarlet red powder (Sp.Gr. 1·876) called scarlet phosphorus. The variety has not been prepared free from the solvent. It resembles red phosphorus but is chemically more active, may be due to its extremely fine state of sub-division.

9. Violet Phosphorus.—It is prepared by crystallization of phosphorus from molten lead. It is a dense variety of phosphorus with a specific gravity 2·34 to 2·39 It does not oxidise in air and is a bad conductor of electricity.

10. Black Phosphorus.—It is prepared by heating white phosphorus to 200°C under 1,000 kg./sq. cm. It is a fairly good conductor of electricity and does not ignite at 400°C.

11. Uses of Phosphorus.—(*i*) In match industry. Formerly yellow phosphorus was used but due to its poisonous nature, it has now been replaced by red phosphorus or *phosphorus trisulphide*, P_4S_3.

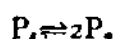
(*ii*) In the manufacture of phosphorus bronze, an alloy of phosphorus, copper and tin.

(*iii*) In the manufacture of incendiary bombs, smoke screens and fireworks.

(*iv*) For the manufacture of compounds, like hypophosphites (used in medicine), phosphorus chlorides (used in chemical industry) and phosphoric acid.

(*v*) White phosphorus is used as a rat poison.

12. Formula of Phosphorus.—White phosphorus has the molecular formula P_4 both in solid and vapour states at moderate temperatures. The four atoms present in the molecule are arranged at the corners of a tetrahedron (Fig 44 5). At higher temperature (above 700°C), however, dissociation to diatomic molecules, P_2 occurs.



$$P_4 \rightleftharpoons 2P_2$$

The structure of red phosphorus has not yet been completely determined, but there is evidence that it is polymeric and consists of chains of P_4 tetrahedra linked together possibly in the manner as shown in Fig. 44·6. As compared with white phosphorus, red phosphorus is less reactive, less volatile and less soluble especially in non-polar solvents, because of its highly polymerized structure.

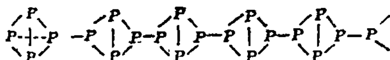


Fig. 44·5. Fig 44 6

13 Phosphorus Cycle.—Like nitrogen, [illegible] growth of plants and animals It is an importa[illegible] derive phosphorus required by them from the [illegible] the source of necessary phosphorus for animals

As a result of death and decay of the bones in cemeteries, phosphorus passes into the soil of rivers. It is also added to the soil in the form of fish manures or phosphatic manures obtained from bones or other sources.

Thus a cycle of changes is repeated by means of which the circulation of phosphorus continues in nature. The phosphorus cycle in nature is summarized below :

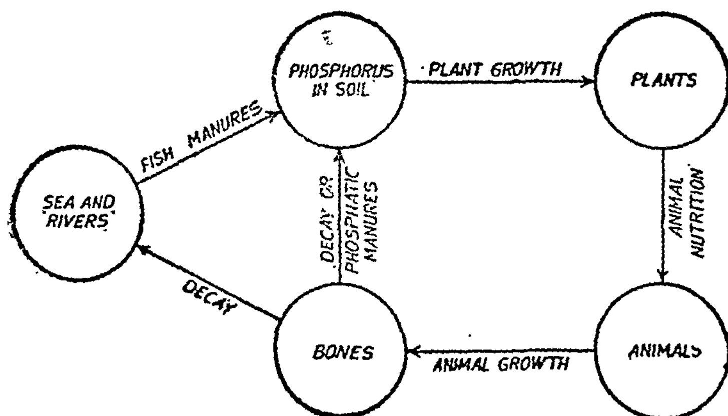


Fig. 44·7—Phosphorus cycle in nature.

14. **Match Industry.**—It is very interesting to go round a match factory and see how from logs of wood matches are manufactured by machinery in an automatic process. Logs of *simbal* or any other wood are moistened and cut into splinters of about two inches length, which are later converted into match-sticks and peelings which are converted into boxes. This is all done by machinery.

The first match factory in India was started with Indian management at Ahmedabad as early as 1895. After 1928 a network of factories was established in Bareilly, Ambernath, Calcutta and Madras by the Western India Match Company Limited and others. At present there are about 50 match factories in India with their total installed annual capacity of 800,000 cases of 50 gross boxes each.

Lucifer and Safety Matches. The two kinds of matches available in the market are :

(1) **Lucifer matches.** These are also called *Friction matches* or *Strike anywhere matches*. These are prepared by dipping the match-sticks successively in three different baths as given below :

(*a*) **First Dip.** The match-sticks are first dipped in a combustible material, *e.g.*, molten sulphur or melted paraffin to about half an inch length.

(*b*) **Second Dip.** At the extreme tip the match-sticks are dipped in a paste consisting of the following constituents :

(*i*) *A readily combustible substance* like antimony trisulphide.

(ii) *A low kindling material* which starts combustion. White phosphorus was previously used for this purpose. Being poisonous, its use is forbidden by law and has, therefore, been replaced by red phosphorus or phosphorus trisulphide.

(iii) *An oxidising agent like* potassium chlorate, potassium nitrate or red lead which supplies oxygen needed for the combustion.

(iv) *An inert substance* to cause friction and decrease sensitiveness, *e.g.*, glass powder or chalk.

(v) *A binding material*, *e.g.*, glue. This binds the various constituents together and enables them to stick to the match head.

(c) **Third Dip.** These are next dipped in molten wax to provide a thin protective coating to the tip of the match-stick.

To prevent after-glow, the match-sticks are impregnated with borax. Match-sticks are boiled with a concentrated borax solution and dried before dipping into match-head composition. Match-sticks thus impregnated with borax are extinguished immediately after they are blown out without glowing for any appreciable time.

How is a lucifer match-stick lighted? The side of the box is coated with a sand and glue mixture. When the match head is rubbed against this or any other rough surface, low kindling material, phosphorus trisulphide, P_4S_3 in this case, catches fire due to heat produced by friction. Easily combustible substance (antimony sulphide) is next lighted. Sulphur is next to burn and finally the match-stick catches fire. Oxidising agent supplies oxygen necessary for combustion.

(2) **Safety matches.** *The composition of* a safety match differs from that of the lucifer match in the fact that low-kindling material is absent from the tip. This is present in the composition pasted on

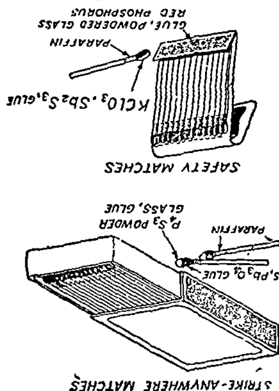


Fig 44 8—The composition of two types of matches.

the side of the box. The paste applied to the side of the box is obtained by mixing red phosphorus or phosphorus trisulphide with sand or glass powder (to cause friction) and glue (binding material).

How is safety match-stick lighted? To light the safety match-stick, it is rubbed against this special surface. A trace of phosphorus is detached and ignited locally by heat due to friction. This tiny spark ignites antimony sulphide, sulphur and match-stick in turn as in lucifer matches.

Lucifer matches which were a cause of many dangerous fires due to accidental friction have now been completely replaced by safety matches.

15. *Position of* Phosphorus in the Periodic Table.—Phosphorus occupies a position under nitrogen in group VA of the periodic table. Its relationship with other elements of the group is discussed briefly on page 2·169. For complete discussion refer to the table in *Chapter* 48.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Bone-ash+Sand+Coke (*Heated in electric furnace*).
2. Bone-ash+Sulphuric acid.
3. Metaphosphoric acid+Coke.
4. Phosphorus+(*i*) Caustic soda, (*ii*) Chlorine, (*iii*) Nitric acid, (*iv*) On burning, (*v*) Sulphur.

QUESTIONS

Essay-type Questions :

1. *How does phosphorus occur in nature ? Describe the electrothermic* process for the manufacture of white phosphorus from calcium phosphate. What is the action of yellow phosphorus with (*i*) caustic soda, (*ii*) sodium metal, (*iii*) sulphuric acid, (*iv*) iodine. Name the products formed in each case. (*Punjab Pre-Univ. 1971*)

2. How is white phosphorus manufactured from bone-ash ? How can it be converted into red phosphorus ? What are safety matches and how are they prepared ? (*Punjab Inter. 1961 ; Punjab H.S. 1962*)

3. How is red phosphorus manufactured ? Describe how you will prepare red phosphorus from the yellow variety. What are the commercial uses of red phosphorus ? What is the difference in the composition of a " strike anywhere" *match-stick and a safety match-stick ?* (*Delhi H.S. 1968, 61*)

4. Describe the extraction of yellow phosphorus from bones. How can it be converted into (*a*) red phosphorus, (*b*) phosphine, (*c*) phosphorus trichloride, (*d*) phosphorus pentachloride, (*e*) phosphoric acid (H_3PO_4), (*f*) P_4O_6, and (*g*) P_4O_{10} ? (*M.P. Inter. 1964*)

5. Describe a method for preparing red phosphorus from white phosphorus on a large scale. How is red phosphorus separated from white phosphorus ?

What happens when both the forms are separately treated as follows ?—

(*i*) Exposed to air, (*ii*) Boiled *with sodium* hydroxide solution, (*iii*) Observed in the dark. (*Nagpur Pre-Univ. 1971*)

6. Justify that N, P, As, Sb and Bi belong to the same family of elements. (*M.P. Board Inter. 1964*

7. Compare and contrast the properties of white and red phosphorus. How would you free a specimen of red phosphorus from traces of white phosphorus ? (*Punjab Pre-Univ. 1964 ; Kashmir Inter. 1961 ; U.P. Board 1960 ; Delhi H.S. 1968, 62*)

8. (*a*) Write a short essay on Match Industry. (*Punjab Pre-Univ. 1971*)

(*b*) What type of matches do you use in everyday life ? Give its advantages over the other type. (*Guru Nanak Pre-Univ. 1971*)

9. Write a short note on phosphorus cycle in nature.

10. Write a short note on allotropy.
(*Delhi H.S. 1965, 62 ; Bihar H.S. 1966, 65 Supp., 63, 61*)

Test Your Understanding

11. Fill in the blanks :

(*a*) Red phosphorus and white phosphorus are .....forms of phosphorus.

(*b*) When bone-ash, sand and coke is heated in an electric furnace vapours of..... are obtained.

(*c*) ... ..phosphorus has very low ignition temperature.

(*d*) .... phosphorus reacts with alkali solutions on heating.

(*e*) When phosphorus is heated with nitric acid it is .....to......

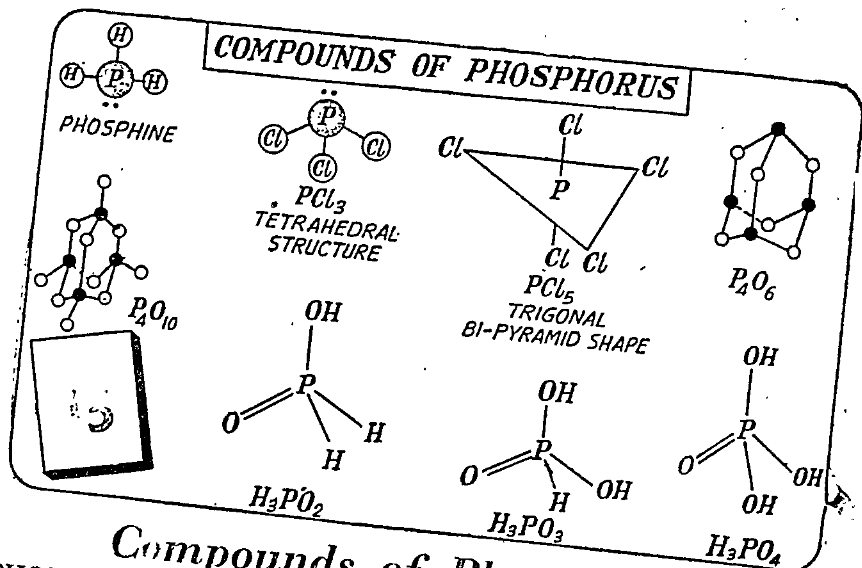
(*f*) Red phosphorus can be converted to white phosphorus by......

(*g*) The stable allotrope of phosphorus is.....

(*h*) Red phosphorus is .....in carbon disulphide.

KEY

11. (*a*) allotropic, (*b*) phosphorus, (*c*) white,
(*d*) white, (*e*) oxidised, phosphoric acid,
(*f*) condensing its vapours under water,
(*g*) red phosphorus, (*h*) insoluble.

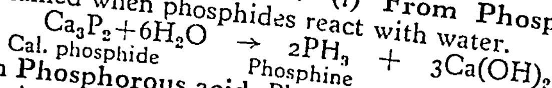


Compounds of Phosphorus

PHOSPHINE

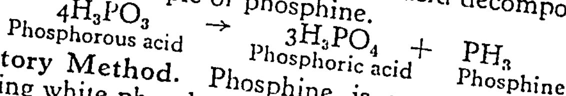
1. **General**—Phosphorus gives two well-defined hydrides viz., phosphine (gaseous phosphorus trihydride or phosphoretted hydrogen) and the liquid phosphorus dihydride (P_2H_4). Phosphine was discovered in 1783 by Gengembre who prepared it by heating white phosphorus with alkali. It is formed by the bacterial reduction of phosphates in the soil and putrefaction of phosphates.

2. **Preparation of Phosphine.**—(*i*) **From Phosphides.** Phosphine is obtained when phosphides react with water.



$$\underset{\text{Cal. phosphide}}{Ca_3P_2} + 6H_2O \rightarrow \underset{\text{Phosphine}}{2PH_3} + 3Ca(OH)_2$$

(*ii*) **From Phosphorous acid.** Phosphorous acid decomposes when heated to give a pure sample of phosphine.



$$\underset{\text{Phosphorous acid}}{4H_3PO_3} \rightarrow \underset{\text{Phosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$$

(*iii*) **Laboratory Method.** Phosphine is prepared in the laboratory by heating white phosphorus with concentrated sodium hydroxide solution in an inert atmosphere of carbon dioxide or oil gas in a round bottom flask (Fig. 45·1). Phosphine evolved is spontaneously inflammable due to the presence of phosphorus dihydride (P_2H_4, the liquid hydride) as impurity. Bubbles of the gas catch fire as soon as they come in contact with air, forming vortex rings of smoke. Pure gas may be obtained using alcoholic potash instead of caustic soda solution.

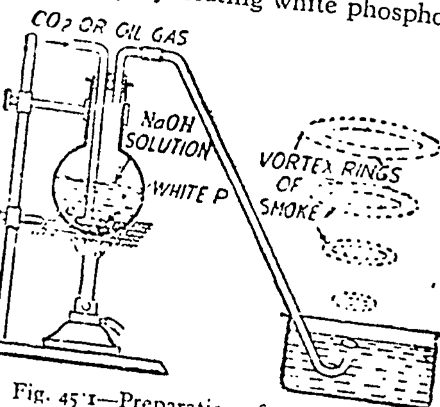
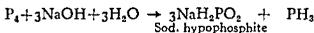
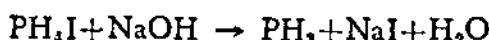


Fig. 45·1—Preparation of phosphine



$$P_4+3NaOH+3H_2O \rightarrow \underset{\text{Sod. hypophosphite}}{3NaH_2PO_2} + PH_3$$

(*iv*) **From Phosphonium Compounds.** A pure sample of phosphine may be prepared by heating phosphonium iodide with caustic soda solution.



$$PH_4I+NaOH \rightarrow PH_3+NaI+H_2O$$

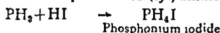
3. **Properties of Phosphine.**

(*a*) **Physical.** (*i*) It is a colourless gas with a disagreeable odour of rotten fish.

(*ii*) It is highly poisonous in nature.

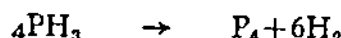
(*iii*) It is somewhat insoluble in water.

(*b*) **Chemical.** (*i*) **Basic Nature.** It is neutral towards litmus but is feebly basic in nature. With acids it reacts to give phosphonium salts which are quite stable (*cf*, ammonium salts).



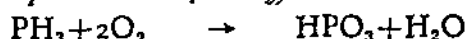
$$PH_3+HI \rightarrow \underset{\text{Phosphonium iodide}}{PH_4I}$$

(*ii*) **Decomposition** When heated out of contact with air to 440°C or when electric sparks are passed through it, phosphine decomposes to give red phosphorus and hydrogen.



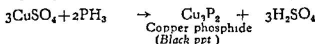
$$4PH_3 \rightarrow P_4+6H_2$$

(*iii*) **Combustibility.** A pure sample of phosphine is not spontaneously inflammable. It burns, however, in air or oxygen to produce metaphosphoric acid (HPO_3) and water.

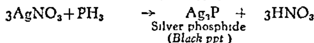


$$PH_3+2O_2 \rightarrow HPO_3+H_2O$$

(*iv*) **With Metallic Salts.** When bubbled through metallic salt solutions, it precipitates corresponding phosphides (*cf*, H_2S).

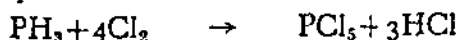


$$3CuSO_4+2PH_3 \rightarrow \underset{\substack{\text{Copper phosphide}\\ (\textit{Black ppt})}}{Cu_3P_2} + 3H_2SO_4$$



$$3AgNO_3+PH_3 \rightarrow \underset{\substack{\text{Silver phosphide}\\ (\textit{Black ppt})}}{Ag_3P} + 3HNO_3$$

(*v*) ***With Chlorine.*** *Phosphine readily burns in chlorine* to give phosphorus pentachloride.

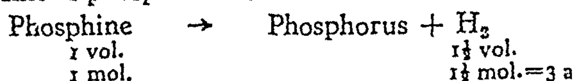


$$PH_3+4Cl_2 \rightarrow PCl_5+3HCl$$

4. **Uses.**—(*i*) *Holme's Signals.* A mixture of calcium carbide and calcium phosphide is taken in a container which is pierced and thrown into the sea. Phosphine liberated catches fire and lights up acetylene. Burning gases serve as a signal to the approaching ships.

(*ii*) *In smoke screens.* Calcium phosphide is used in smoke screens. Phosphine obtained catches fire to give the needed smoke.

5. **Composition of Phosphine.**—Electric sparks are pa through a known volume of phosphine enclosed over mercury eudiometer tube. The volume of hydrogen obtained is found t $1\frac{1}{2}$ times the volume of phosphine taken.



By applying Avogadro's law, we learn that one molecul phosphine yields $1\frac{1}{2}$ molecule (=3 atoms) of hydrogen and atoms of phosphorus (say, x). Thus the formula of phosphi P_xH_3 with molecular weight$=31x+3$.

Equating this with molecular weight of phosphine (determined experimentally, we have

$$31x+3=34 \qquad \text{whence} \qquad x=1$$

Hence molecular formula of phosphine is PH_3.

6. **Comparison of Phosphine with Ammonia.**

(*a*) **Points of resemblance of the two hydrides :**

(i) Both the hydrides have similar chemical constitution, *viz.*, NH PH_3.

(*ii*) Both are easily decomposed into elements by electric sparks.

(*iii*) With halogen acids both give similar compounds—phosph (PH_4I) and ammonium (NH_4I) salts. These liberate the hydride again heated with caustic soda or potash.

(*iv*) *With chlorine, both of them react violently.*

(*v*) In air they burn when heated.

(*b*) *Points of difference :*

(*i*) Ammonia is quite stable while phosphine is much less stable.

(*ii*) *Phosphine is insoluble in water while ammonia is highly solub*

(*iii*) Phosphine is neutral towards litmus while ammonia is alkaline.

(*iv*) Phosphine has a fishy odour *(disagreeable) while ammonia* characteristic pungent smell.

(*v*) Phosphine is poisonous while ammonia is not so.

(*vi*) Phosphine precipitates phosphides from metallic salt solutions with ammonia the hydroxides are precipitated.

(*vii*) Ammonium salts are *quite stable while phosphonium salts* are less stable.

PHOSPHORUS HALIDES

7. **General.**—With halogens phosphorus gives two of halides, the trihalides and the pentahalides. For example, chlorine it gives phosphorus *trichloride and phosphorus* p chloride.

8. **Phosphorus trichloride, PCl_3.**

Preparation. *This is* prepared *by* heating white phosp

...tort on a water-bath and a ...·2). Phosphorus trichloride collected in a receiver cooled in freezing mixture.

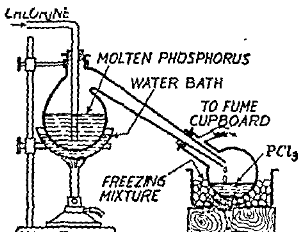
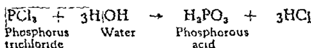


Fig. 45·2—Preparation of phosphorus trichloride.

It is redistilled over white phosphorus to remove any phosphorus pentachloride present as impurity.

Properties. (i) It is a colourless mobile liquid (b.p. 79°C, f.p.=−112°C; Sp. Gr. 1·6) with a pungent smell.

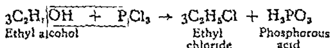
(ii) It fumes in moist air and reacts with water violently to give phosphorous acid.



$$PCl_3 + 3H\,OH \rightarrow H_3PO_3 + 3HCl$$

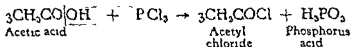
Phosphorus trichloride, Water, Phosphorous acid

(iii) It reacts with organic compounds containing hydroxyl (−OH) group, *e.g.*, acetic acid (CH_3COOH) and alcohol (C_2H_5OH). In each case the hydroxyl group is replaced by a chlorine atom and phosphorous acid is produced.



$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

Ethyl alcohol, Ethyl chloride, Phosphorous acid



$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$$

Acetic acid, Acetyl chloride, Phosphorus acid

(*iv*) With chlorine, it combines forming phosphorus pentachloride.



$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Uses. It finds use in organic chemistry for replacing hydroxyl group by chlorine atoms.

9. Phosphorus Pentachloride, PCl_5.

Preparation. Phosphorus pentachloride is prepared by the action of dry chlorine (*excess*) on phosphorus trichloride.



$$PCl_3 + Cl_2 \rightarrow PCl_5$$

Phosphorus trichloride is slowly dropped from a dropping funnel into a flask cooled in freezing mixture (Fig. 45·3) while a current of dry chlorine is passed in. At the end, excess of chlorine is swept out with a current of carbon dioxide and flask is corked.

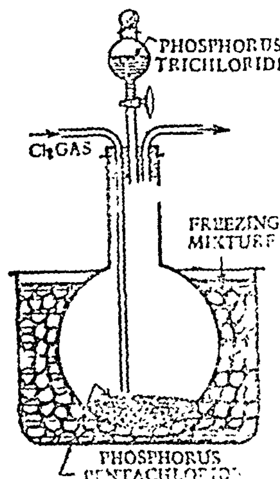


Fig. 45·3—Preparation of phosphorus pentachloride.

Properties. (*i*) It an almost colourless crystalline solid with a pungent odour when pure. As obtained in the laboratory it is usually pale greenish yellow in colour.

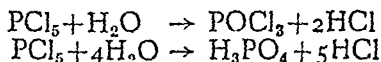
(*ii*) On heating. it sublimes below 100°C and can be melted (m.p. 148°) only by heating under pressure.

(*iii*) *Dissociation*. It is inferred from its vapour density data that phosphorus pentachloride dissociates on heating into phosphorus trichloride and free chlorine.



$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(*iv*) *With water*, it combines violently forming phosphorus oxychloride, $POCl_3$ (with insufficient water) and phosphoric acid, H_3PO_4 (with excess of water).



$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$
$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

(*v*) *With hydroxyl compounds*, it reacts and replaces the hydroxyl groups by chlorine atoms. For example,



$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + PCl_5 \rightarrow \underset{\text{Ethyl chloride}}{C_2H_5Cl} + POCl_3 + HCl$$



$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$



$$\underset{\text{Sulphuric acid}}{SO_2(OH)_2} + 2PCl_5 \rightarrow \underset{\text{Sulphuryl chloride}}{SO_2Cl_2} + 2POCl_3 + 2HCl$$

Uses. It is extensively used in organic chemistry for replacement of hydroxyl groups by chlorine atoms.

OXIDES OF PHOSPHORUS

10. **General.**—Phosphorus is known to give three definite oxides. These are :

(*i*) Phosphorus trioxide, also called phosphorous oxide, P_4O_6.

(*ii*) Phosphorus tetroxide, P_2O_4.

(*iii*) Phosphorus pentoxide, P_4O_{10}.

11. **Phosphorus trioxide, P_4O_6.**

Preparation. A mixture of phosphorus trioxide and phosphorus pentoxide is obtained when phosphorus is burnt in a limited supply of air.

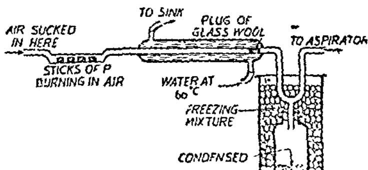


Fig. 45 4—Preparation of phosphorus trioxide.

Sticks of yellow phosphorus are placed in a bent tube connected with a Liebig's condenser and a U-tube as shown (Fig. 45 4).

Phosphorus is ignited and air is sucked through the bent tube with the help of an aspirator attached to the U-tube and water at 60°C is circulated through the condenser. Phosphorus pentoxide (solid at 66°C) is kept back by a plug of glass wool placed in the way whereas phosphorus trioxide vapours pass on and are condensed in the receiver cooled in freezing mixture.

Properties. (i) It is a crystalline solid (m.p. 22·5°C ; b.p. 173°C) with strong garlic odour.

(ii) Its vapour density (≈110) corresponds to the formula P_4O_6.

(iii) It is poisonous in nature.

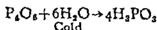
(iv) In contact with air, it is slowly oxidised to phosphorus pentoxide whereas in contact with warm oxygen, it bursts into a flame.



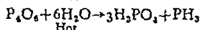
$$P_4O_6+2O_2 \rightarrow P_4O_{10}$$

(v) In chlorine also it burns spontaneously forming $POCl_3$ and another product perhaps PO_2Cl—metaphosphoryl chloride.

(vi) In cold water it dissolves slowly to give phosphorous acid whereas in hot water it gives phosphoric acid and phosphine.



$$P_4O_6+\underset{\text{Cold}}{6H_2O} \rightarrow 4H_3PO_3$$



$$P_4O_6+\underset{\text{Hot}}{6H_2O} \rightarrow 3H_3PO_4+PH_3$$

12. **Phosphorus pentoxide, P_4O_{10}.**

Preparation. Phosphorus pentoxide is prepared by burning phosphorus in an excess of dried air or oxygen. White clouds of the oxide are condensed to snowy powder. It is purified by heating (600-700°C) in a rapid stream of air. Phosphorus pentoxide vaporizes and the vapours are condensed.

Properties. (i) It is white solid which sublimes on heating. It is odourless when pure. The garlic odour of a common sample is due to the presence of P_4O_6.

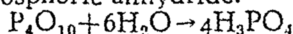
(ii) Its vapour density corresponds to the formula P_4O_{10} but molecular weight of the solid is not known.

(iii) It has a great affinity for water. It dissolves in cold water with a hissing sound and metaphosphoric acid is formed.



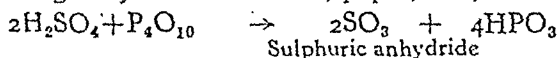
$$P_4O_{10}+2H_2O \rightarrow 4HPO_3$$

With hot water, is gives ortho phosphoric acid, H_3PO_4. It is, therefore, termed phosphoric anhydride.

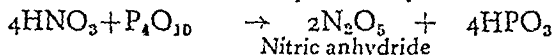


$$P_4O_{10}+6H_2O \rightarrow 4H_3PO_4$$

(iv) It is a strong dehydrating agent and removes a molecule of water from a large number of inorganic and organic compounds. For example, sulphuric acid and nitric acid are converted into their corresponding anhydrides and wool, paper, etc., are charred.



$$2H_2SO_4+P_4O_{10} \rightarrow \underset{\text{Sulphuric anhydride}}{2SO_3} + 4HPO_3$$



$$4HNO_3+P_4O_{10} \rightarrow \underset{\text{Nitric anhydride}}{2N_2O_5} + 4HPO_3$$

Uses. It is used as a valuable drying and dehydrating agent.

OXY-ACIDS

13. **General.**—The more important oxy-acids of phosphorus are :

(i) Hypophosphorous acid, H_3PO_2. It is monobasic and gives salts of the formula NaH_2PO_2, sodium hypophosphite.

(ii) Phosphorous acid, $H_3PO_3(P_4O_6.6H_2O)$.

(iii) Hypophosphoric acid, $H_4P_2O_6$ $(P_2O_4.2H_2O)$.

(iv) Orthophosphoric acid, $H_3PO_4(P_4O_{10}.6H_2O)$.

(v) Metaphosphoric acid, $HPO_3(P_4O_{10}.2H_2O)$.

(vi) Pyrophosphoric acid, $H_4P_2O_7(P_4O_{10}.4H_2O)$.

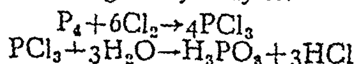
14. **Phosphorous acid**

Preparation. (i) *By dissolving phosphorus trioxide in cold water.*



$$P_4O_6+6H_2O \rightarrow 4H_3PO_3$$

(ii) *By hydrolysis of phosphorus trichloride.* Chlorine is passed into phosphorus melted under water when phosphorus trichloride first formed undergoes hydrolysis.

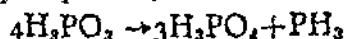


$$P_4+6Cl_2 \rightarrow 4PCl_3$$
$$PCl_3+3H_2O \rightarrow H_3PO_3+3HCl$$

Properties. (i) It crystallizes as white solid (m.p. 70°C) soluble in water.

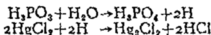
(ii) It is a dibasic acid normally and gives the salts called phosphites.

(iii) *Action of Heat.* On heating, it decomposes giving orthophosphoric acid and phosphine (*Auto-oxidation*).

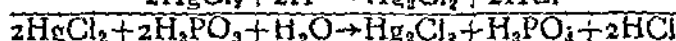


$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$$

(iv) *Reducing agent.* The ease, with which it picks up an atom of oxygen, renders it a strong reducing agent. It reduces mercuric salts to mercurous salts and gold, silver and cupric salts to the metals.



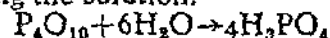
$$H_3PO_3 + H_2O \rightarrow H_3PO_4 + 2H$$
$$2HgCl_2 + 2H \rightarrow Hg_2Cl_2 + 2HCl$$



$$2HgCl_2 + 2H_3PO_3 + H_2O \rightarrow Hg_2Cl_2 + H_3PO_4 + 2HCl$$

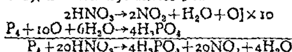
15. **Orthophosphoric acid, H_3PO_4.**

Preparation. (i) By dissolving phosphorus pentoxide in water and boiling the solution.



$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

(ii) By oxidation of red phosphorus with concentrated nitric acid in the presence of a flake of iodine (*catalyst*). On evaporation (below 180°C), the acid crystallizes out.



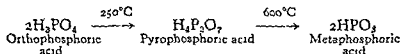
$$[2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 10$$
$$P_4 + 10O + 6H_2O \rightarrow 4H_3PO_4$$
$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(iii) *Manufacture.* It is prepared on a commercial scale by the action of concentrated sulphuric acid on calcium phosphate or bone-ash (*see* page 2·203) or by oxidation of phosphorus vapour obtained by the electric furnace method (*see* page 2 202). Phosphorus pentoxide obtained as a result of oxidation is dissolved in water.

Properties. (i) It is a transparent, deliquescent, crystalline solid (m.p. 42°C) which absorbs water and gives a colourless syrupy liquid.

(ii) *Acidic nature.* It dissolves in water giving feebly acidic solution. With alkalis, it gives three series of salts, *e.g.*, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4.

(iii) *Action of heat.* On heating it loses a molecule of water at 250°C to give pyrophosphoric acid which on further heating to 600°C loses another molecule of water and gives metaphosphoric acid.



$$2H_3PO_4 \xrightarrow{250°C} H_4P_2O_7 \xrightarrow{600°C} 2HPO_3$$

Orthophosphoric acid — Pyrophosphoric acid — Metaphosphoric acid

Uses. (i) In medicine.

(ii) In the preparation of hydrobromic and hydriodic acids.

(iii) In the manufacture of phosphorus, phosphates and concentrated forms of phosphatic manures.

16 **Orthophosphates or Phosphates.**—These are salts of orthophosphoric acid. These are termed primary, secondary and tertiary respectively as one, two or three hydrogen atoms of the acid are replaced by basic radicals.

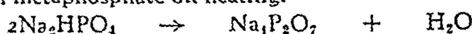
General Properties and Tests. (i) *Solubility.* Phosphates of alkali metals are soluble in water. Others, which are insoluble in water, readily dissolve in dilute acids.

(ii) *Action of Heat.* They swell on heating. Further normal or tertiary phosphates, *e.g.*, Na_3PO_4 and $Ca_3(PO_4)_2$ are not decomposed by heat. Magnesium ammonium phosphate is an exception and gives pyrophosphate on heating.

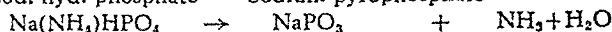


$$\underset{\text{Mg. amm. phosphate}}{2MgNH_4PO_4} \rightarrow \underset{\text{Mag. pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

Secondary phosphates (monohydrogen phosphates) are decomposed and yield pyrophosphates. Microcosmic salt (sodium ammonium hydrogen phosphate) gives sodium metaphosphate on heating.



$$\underset{\text{Disod. hyd. phosphate}}{2Na_2HPO_4} \rightarrow \underset{\text{Sodium pyrophosphate}}{Na_4P_2O_7} + H_2O$$



$$\underset{\text{Microcosmic salt}}{Na(NH_4)HPO_4} \rightarrow \underset{\text{Sod. metaphosphate}}{NaPO_3} + NH_3+H_2O$$

Here we find that ammonium radical in phosphates behaves like a hydrogen atom. Primary (or dihydrogen) phosphates give metaphosphates on heating.



$$NaH_2PO_4 \rightarrow NaPO_3+H_2O$$

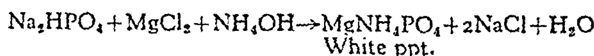
(iii) *Charcoal cavity Test.* When heated with a drop of cobalt nitrate on a charcoal cavity, it gives a blue mass.

(iv) *Ammonium molybdate Test.* When heated with ammonium molybdate and a few drops of concentrated nitric acid, it gives a yellow precipitate or coloration of ammonium phospho-molybdate, $(NH_4)_3PO_4.12\ MoO_3.6H_2O$ on cooling.

(v) *Silver nitrate Test.* On adding silver nitrate to a normal solution, a phosphate gives yellow precipitate which is soluble both in nitric acid as well as ammonium hydroxide.

(vi) *Ferric chloride Test.* With ferric chloride, a neutral solution of a phosphate gives yellow precipitate insoluble in acetic acid but soluble in hydrochloric acid.

(vii) *Magnesia mixture Test.* On adding magnesia mixture to an aqueous solution of a phosphate we get a white precipitate of magnesium ammonium phosphate.



$$Na_2HPO_4+MgCl_2+NH_4OH \rightarrow \underset{\text{White ppt.}}{MgNH_4PO_4}+2NaCl+H_2O$$

(vii) *With cobalt nitrate,* phosphates in neutral solution give a violet blue precipitate soluble in acetic acid.

Estimation. For estimation, a known weight of a phosphate (say, *w* gm.) is dissolved in water or dilute acid and precipitated as magnesium ammonium phosphate. This is filtered, washed, dried and ignited to constant weight (say, W) when we get magnesium pyrophosphate. From the weight of magnesium pyrophosphate, $Mg_2P_2O_7$ (Mol. wt.=222, obtained from two phosphate radicals weighing $2\times95=190$) we can calculate the percentage of phosphate radical.

$$\text{Percentage of phosphate}=W\times\frac{190}{222}\times\frac{100}{w}.$$

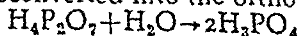
17. Pyrophosphoric acid, $H_4P_2O_7$.—It is prepared by heating orthophosphoric acid to 250—260°C.



$$2H_3PO_4 \rightarrow H_4P_2O_7+H_2O$$

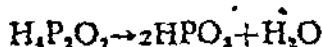
Properties. (i) It is a colourless solid (m.p. 61°C).

(ii) It is soluble in water and on boiling the aqueous solution, pyro-acid is reconverted into the ortho-acid.



$$H_4P_2O_7+H_2O \rightarrow 2H_3PO_4$$

(iii) On strong heating, pyrophosphoric acid gives metaphosphoric acid.



$$H_4P_2O_7 \rightarrow 2HPO_3 + H_2O$$

(iv) It is a tetrabasic acid but gives rise to only two series of salts, *e.g.*, $Na_2H_2P_2O_7$ and $Na_4P_2O_7$.

18. Pyrophosphates.—These are obtained by heating secondary phosphates, e g, Na_2HPO_4 or normal phosphates containing one ammonium radical (see page 2·220).

They give a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$ with [illegible] precipitate of cobalt [illegible] solution. They do [illegible]

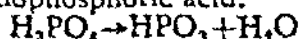
[illegible]

Preparation. (i) By dissolving phosphorus pentoxide in a little of cold water.



$$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$$

(ii) By igniting orthophosphoric acid.



$$H_3PO_4 \rightarrow HPO_3 + H_2O$$

Properties. (i) It is a transparent glassy solid and is, therefore, generally called *glacial phosphoric acid.*

(ii) It is a deliquescent solid, soluble in water. On boiling the aqueous solution, it is reconverted into the ortho acid.



$$HPO_3 + H_2O \rightarrow H_3PO_4$$

(iii) It is a mono-basic acid (fairly strong) and its salts are termed metaphosphates.

(iv) It coagulates albumen.

20. Metaphosphates.—These are prepared by heating dihydrogen phosphates (primary) or monohydrogen ammonium phosphate (see page 2 220).

Properties. (i) These are transparent glassy solids having colours characteristic of the metal radical (*Microcosmic bead test*).

(*ii*) *Their aqueous solutions give white gelatinous precipitate* with silver nitrate but no precipitate with magnesia mixture or cobalt nitrate solution.

(iii) With an acidic solution of barium chloride, they give a white precipitate (*difference from phosphates*).

21. Distinguishing Tests of the three phosphoric acids.

Reagent	Ortho- H_3PO_4	Pyro- $H_4P_2O_7$	Meta- HPO_3
1. Magnesia mixture	White ppt insoluble in excess	White ppt soluble in excess.	No ppt.
2. Silver nitrate	Yellow ppt. soluble in NH_4OH and HNO_3 both	White crystalline ppt	White gelatinous ppt.
3 White of an egg	No action.	No action.	Coagulated
4. Ammonium molybdate $+HNO_3$	Yellow ppt.	No action.	Yellow ppt
5. Cobalt nitrate	Violet blue ppt	Pink ppt.	No ppt.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Calcium phosphide+Water.

2. Phosphorous acid+(*i*) Heated, (*ii*) Mercuric chloride.

3. Phosphorus+(*i*) Caustic soda, (*ii*) Chlorine.

4. Phosphonium iodide+Caustic soda.

5. Phosphine+(*i*) Hydriodic acid, (*ii*) Hydrochloric acid, (*iii*) heated, (*iv*) burnt, (*v*) Copper sulphate, (*vi*) Silver nitrate, (*vii*) Chlorine.

6. Phosphorus trichloride+(*i*) Water, (*ii*) Alcohol, (*iii*) Organic acid, (*iv*) Chlorine.

7. Phosphorus pentachloride+(*i*) Water, (*ii*) Ethyl alcohol, (*iii*) Acetic acid, (*iv*) Sulphuric acid, (*v*) Heated.

8. Phosphorus trioxide+(*i*) Oxygen, (*ii*) Water—cold and hot.

9. Phosphorus pentoxide (*i*) Water—cold and hot, (*ii*) Sulphuric acid, (*iii*) Nitric acid.

10. Action of heat on (*i*) Orthophosphoric acid, (*ii*) Trisodium phosphate, (iii) Disodium hydrogen phosphate, (*iv*) Magnesium ammonium phosphate, (*v*) Monosodium dihydrogen phosphate, (*vi*) Microcosmic salt, (vii) Pyrophosphoric acid.

QUESTIONS

Essay-type Questions

1. (*a*) How is phosphine usually prepared in the laboratory ? Give details with necessary equations. Mention the precautions that must be taken for its preparation.

(*b*) How can you prepare pure phosphine ?

(*c*) Compare the properties of phosphine and ammonia.
(*Nagpur Pre-Univ. 1971 ; Guru Nanak 1971*)

2. Describe the laboratory preparation of phosphine and ammonia gas. In what respects do these two hydrides resemble and differ from one another ? How would you distinguish one from the other ?

3. How is phosphine prepared in the laboratory ? How does it react with (i) chlorine, (ii) copper sulphate ? (*Punjab Pre-Univ. 1970*)

4. Give formulae of (*a*) orthophosphoric acid, (*b*) pyrophosphoric acid, and (*c*) metaphosphoric acid.

How is orthophosphoric acid prepared from (*i*) bone-ash, (*ii*) phosphorus, and how is it converted into the other two acids ? What tests may be used to identify these acids ? (*Delhi Pre-Medical 1961*)

5. Give the preparation and properties of any two of the following :

(i) Phosphorus trichloride, (*ii*) Phosphorus trioxide,

(iii) Phosphorus pentachloride, (*iv*) Phosphorus pentoxide.

(*All India H.S. 1971, 67 ; Punjab Pre-Univ. 1969 ; Delhi H.S. 1972, 71, 69, 67 ; Delhi Prep. 1960*)

6. How will you distinguish between an orthophosphate and a metaphosphate ? Give equations where necessary. (*Punjab Inter. 1960*)

Test Your Understanding :

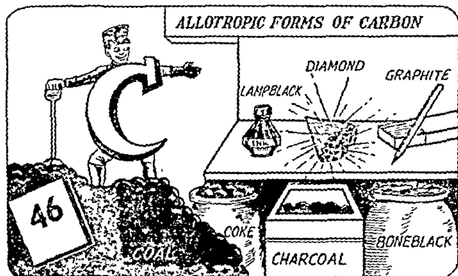
7. What happens when :

(*a*) Phosphorus trichloride is reacted with water.

(*b*) White phosphorus is added to a hot solution of caustic potash.

(*c*) Phosphorus pentachloride reacts with water.

(*d*) Phosphine is passed into copper sulphate.



Carbon

1. **Historical.**—Various forms of carbon, *e.g.*, charcoal, soot, times. Issac Newton must be combustible. on dioxide was formed when diamond was burnt in oxygen. Smithson Tennant, an English chemist, proved in 1797 that diamond is pure carbon.

2. **Occurrence.**—Carbon is an abundant element and ranks twelfth in the order of abundance among the elements present in the earth's crust. In the elementary form it occurs as diamond, graphite and amorphous (*without definite shape*) carbon. In the

3. **Allotropic Forms of Carbon.**—We have already learnt that several elements, *e.g.*, sulphur and phosphorus, exist in allotropic forms. Carbon is such an element and its various allotropic forms are :

(1) *Diamond*, a beautiful crystalline form ;

(2) *Graphite*, a soft greyish black crystalline substance ; and

(3) *Amorphous carbon*, black residue left when carbon com- carbon are : l, (*iv*) Bone black, (*vii*) Gas carbon, and (*viii*) Petroleum coke.

4. **Diamonds.**—At one time India was famous for diamonds. Koh-i-Noor (186 carats originally) and the Pitt (136·25 carats) were mined in India. Brazil is known for black diamonds.

Diamond mines are there in Australia too but the most famous ones are located in South Africa. The Cullinan diamond, the largest ever found, weighed 3025·75 carats (about 1·33 pounds) and was mined in South Africa in January, 1905. Diamonds are weighed in carats (1 *carat*=200 *mgm*.).

Properties of Diamonds. (*i*) The diamond is the densest and the hardest variety of carbon (Density=3·51).

(*ii*) In the natural form they do not have the shape or lustre we are familiar with. These have to be cut and polished to enhance their beauty.

(*iii*) These are transparent to light and X-rays and possess high refractive index (=2·45).

(*iv*) Value of a diamond depends on its size as well as colour, Bluish-white diamonds fetch more price than those with yellowish tinge. Certain flaws, *e.g.*, due to faulty cutting or to specks of carbon embedded in them, lower their value. Black diamonds are not suitable as gems.

(*v*) These are bad conductors of heat and electricity and burn only on strong heating in oxygen when nothing but carbon dioxide is obtained. At red heat they burn to graphite. In ordinary solvents these are insoluble.

Uses of Diamonds (*i*) These are used as precious stones for jewellery due to their ability to reflect and refract light. This makes them usually brilliant.

(*ii*) Due to their hardness, black diamonds are used for sawing marble, cutting glass, as rock drills, phonograph needles and as an abrasive.

(*iii*) Diamond dies are used for drawing thin wires. Tungsten wires of diameter less than one-sixth the diameter of human hair have been drawn.

Diamonds cannot be manufactured profitably. Natural diamonds are considered to have been formed under the surface of earth by crystallization of carbon from molten mass under huge pressure prevailing there. Henry Moissan, a French chemist (1852—1907), attempted to obtain diamonds artificially. He dissolved some carbon (sugar charcoal) in molten iron at about 4000°C and plunged the molten mass into molten lead m.p. 327°C). The outer surface of iron cooled quickly and solidified. Later on as molten iron inside the solid ball began to solidify, it expanded and thus exerted huge pressure.

Moissan broke the iron ball after cooling and is reported to have seen tiny diamonds under a microscope. It is doubtful that these particles were diamonds and not particles of iron carbide, a hard substance. The attempt was thus of no value except as an interesting scientific experiment.

5. **Graphite.**—It is found widely distributed in nature, *e.g.*, is Siberia, Ceylon, U.S.A., Canada and Czechoslovakia. Large quantities of graphite are manufactured from coke or anthracite in electric furnaces.

Manufacture of Graphite. Artificial graphite is now made [illegible] cheson, an [illegible] or anthra- [illegible] resistance [illegible] rectangular fire-brick furnace fitted with two electrodes joined by a central core of loose pieces of carbon. Heat H is produced due to the resistance R offered by carbon core to the passage of current, $C(H = CR^2t$, where t is the time).

Heat accumulates in the bed of coke surrounding the central core and results in high temperature and the intense heat converts coke into graphite. It is believed that silicon carbide first formed as an *intermediate* product decomposes at higher temperature to give graphite and silicon, the temperature being high enough to volatilize off silicon.

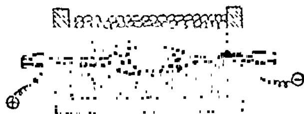
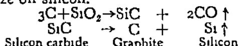


Fig. 46·1—Manufacture of graphite.



$$3C + SiO_2 \rightarrow SiC + 2CO\uparrow$$

$$\underset{\text{Silicon carbide}}{SiC} \rightarrow \underset{\text{Graphite}}{C} + \underset{\text{Silicon}}{Si\uparrow}$$

Properties. (*i*) It is a dark grey substance with characteristic greasy feel and metallic lustre.

(*ii*) It crystallizes in hexagonal plates and varies in specific gravity from 2 to 3.

(*iii*) It marks paper black like lead and was, therefore, called *black lead* or *plumbago*. "Lead" of a lead pencil is mainly a mixture of graphite with variable quantities of clay depending upon the hardness required.

(*iv*) It is a good conductor of heat and electricity.

(*v*) Chemically it is rather inactive and somewhat difficult to ignite. When heated in the absence of air and oxygen, it remains unchanged but burns when heated in air or oxygen and gives carbon dioxide.

(*vi*) When heated with concentrated nitric acid repeatedly, a yellow mass called graphitic acid is obtained. Graphitic acid is insoluble in water and its composition is not quite clear.

Uses. (*i*) It makes a very good lubricant for machine parts subjected to high temperature. Ordinary oil lubricants are charred and cause friction. It is used as such or as graphite grease, graphite mixed with petroleum jelly. *Aqua-dag* and *Oil dag* are suspensions of graphite in water and in oil, respectively, widely used as lubricants.

(*ii*) In the manufacture of refractory crucibles used for high temperature.

(*iii*) For making electrodes of electric furnaces.

(*iv*) For making a non-conducting surface (*e.g.*, wax impression or printer's type); a conductor of electricity in electrotyping or electroplating. Powdered graphite is dusted over the surface.

(*v*) In the manufacture of lead pencils, by mixing powdered graphite with clay and pressing into sticks.

(*vi*) For making stove polish and paints to be used round furnaces because it does not burn off easily.

Structures of diamond and graphite. The atoms of carbon in diamond are arranged in a series of interlacing hexagons to form a 'giant molecule' in which each carbon atom is joined to four others by covalent linkages (*see* Fig. 46·2). These covalent links run without a break. This structure explains some of the most striking properties of diamond, for example, its hardness, great resistance to melting and extreme lack of volatility. The hardness results from the strength of C—C bond and uniformity of bonding and it is the hardest substance known. Similarly as the temperature rises, the vibrational energy of the atoms is not great enough to break strong C—C bonds. Diamond does not, therefore, melt. At 3500°C the vibrational energy is so great that the C—C bonds begin to break away and the diamond vaporises. The C—C bond distance is rather short in diamond which explains its high density (3·51 gm./c.c.).

Structure of graphite consists of a series of layers, each one atom thick, in which the carbon atoms are joined together in hexagonal rings (*see* Fig. 46·3). Since there are no covalent linkages between the adjacent planes, graphite can be easily cleaned along the lines of the planes. It should, however, be noted that a plane itself cannot be easily split up, only the various planes are separable from one another. This structure accounts for the softness and lubricating power of graphite. Graphite is a conductor of electricity which is due to the fact that on account of all the carbon bonds being not satisfied, some of the electrons are free to move through the crystal.

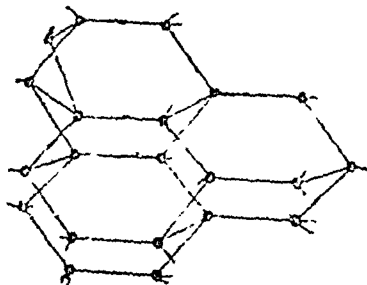


Fig. 46·2—Crystal of diamond.

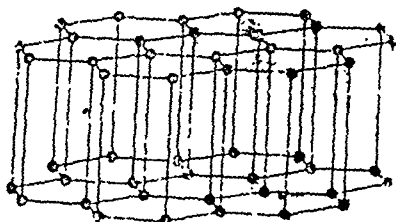


Fig. 46·3—Graphite crystal

6. **Coal.**—Coal is believed to have been formed by the slow carbonization of vegetable matter buried underneath the earth centuries ago, in limited supply of air under high temperature and

pressure prevailing there. The different varieties of coal available, *viz*, *Peat* (60 per cent carbon), *Lignite* (70 per cent carbon), *Bituminous* (78 per cent carbon), *Semi bituminous* (83 per cent carbon) and *Anthracite* (90 per cent carbon) are different stages in the process of carbonization. This view has been confirmed by a microscopic examination of coal. We see that during the progressive stages of metamorphosis, the carbon content steadily increases from 40 per cent in wood to 60, 70, 78, 83 and 90 per cent respectively in different varieties of coal.

The common variety of coal is bituminous. It is hard like stone and burns with a smoky flame. The superior quality coal which burns without any smoky flame is anthracite. Fairly large quantities of coal are available in West Bengal and Bihar.

Its chief uses. Coal is mainly used : (*i*) As a fuel.

(*ii*) For the manufacture of coal gas and various by-products—coke, ammoniacal liquor and coal-tar (source of a large number of organic compounds, *e.g.*, dyes, explosives, chemicals).

(*iii*) In the manufacture of fuel gases—producer gas, water gas, semi-water gas.

(*iv*) In the manufacture of synthetic petrol by catalytic hydrogenation of coal.

7. **Coke.**—When coal is subjected to destructive distillation, it loses several volatile constituents, *e g.*, coal gas, ammonia, benzene, phenol and tar, and the residue left behind is coke. It contains all the mineral matter of coal but is composed of free carbon primarily. Thus coke is coal *minus* volatile matter. It is a pure variety of carbon (80 to 95 per cent carbon).

Prior to 1915, destructive distillation of coal was carried out for the manufacture of coke but today coke is only a by-product.

Uses. Coke is chiefly used :

(*i*) As a reducing agent in the iron and steel industry.

(*ii*) It burns without smoke and is used as a fuel.

(*iii*) For making water gas and graphite.

8. **Charcoal.**—Charcoal is obtained when wood is heated strongly without access to air. Formerly logs of wood were piled up in a pit leaving air spaces at a few places (Fig. 46·4). This was covered with earth and fired. Part of the wood burnt and heated the rest in a limited supply of air. The volatile products were allowed to escape into air and charcoal was obtained.

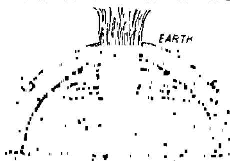


Fig. 46·4—Manufacture of charcoal.

Today charcoal is obtained by heating wood in big closed retorts (Fig. 46·5). The liquid by-products, *viz.*, wood alcohol and acetic acid, are condensed as they pass through a condenser at the top and collect in a storage tank below. The combustible gases which fail to condense are used as fuel for heating the retorts. The residue left in the retorts is charcoal.

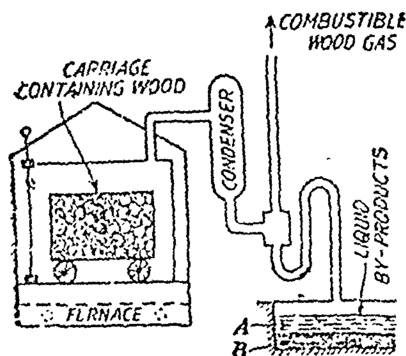


Fig. 46·5– Destructive distillation of wood.

Properties. (*i*) Charcoal is black, porous, brittle solid.

(*ii*) It is heavier than water (Sp. Gr. 1·5) but floats in it due to large quantity of air absorbed in its pores. If, however, charcoal is made red hot (to expel all air) and thrown in water, it sinks.

(*iii*) It absorbs colouring matter and odoriferous gases. It is, therefore, used in decolorising sugar solution and in gas masks. Coconut charcoal is treated with steam to increase its ability to adsorb gases and is said to be **activated.**

The volume of a gas adsorbed by charcoal depends upon :

(*a*) *Temperature of charcoal.* Volume of the gas adsorbed increases with decrease of temperature, *e.g.*, charcoal cooled in liquid air is used for removing residual gases while producing high vacuum.

(*b*) *Nature of the gas.* Gases with higher boiling points are absorbed more than others. Poisonous gases are easily condensed and thus readily adsorbed.

(*c*) *Nature of charcoal.* Activated charcoal is a better adsorbent than ordinary one.

(*iv*) It burns in air to give carbon dioxide with traces of carbon monoxide and thus makes a good fuel.

(*v*) It is good reducing agent.

Uses. Charcoal is used : (*i*) As a fuel.

(*ii*) As a deodorant and decolorising agent. In purification of water, decolorising sugar solution and in gas masks.

(*iii*) As a constituent of gun-powder.

9. **Boneblack or Animal Charcoal.**—Boneblack is left as a residue when bones are subjected to destructive distillation in a retort. *Bone oil and pyridine* are obtained as by-products.

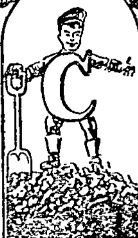
Properties and Uses. (*i*) It is more easily wetted by liquids than wood charcoal. It is, therefore, more suitable as an adsorbent than wood charcoal and is being extensively used for decolorising liquids, *e.g.*, crude sugar solution.


ALLOTROPIC
FORMS OF CARBON
BONEBLACK

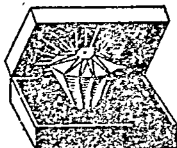



COKE


INK
LAMPBLACK


C
COAL


GRAPHITE


DIAMOND

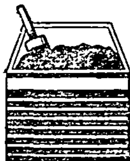

CHARCOAL

Fig 46·6.

(*ii*) On burning it gives bone-ash which is calcium phosphate chemically. Bone-ash is used for the manufacture of phosphorus and phosphoric acid.

10. **Lampblack.**—It is manufactured by burning oils (rich in carbon) in an insufficient supply of air and depositing the soot on wet blankets hung in a room.

It is a velvety black powder used in the manufacture of Indian ink, printer's ink, black paints and varnishes and carbon papers.

11. **Carbon black.**—It is prepared by burning natural gas in limited supply of air and differs from lampblack in being not so greasy. Soot from the burning gas is deposited on the underside of a revolving disc and then scraped off and stored in bags.

It is added to the rubber mix used for making automobile tyres, and has replaced lampblack used for a number of purposes.

12. **Gas carbon and Petroleum coke.**—Carbon scraped from the walls of the retorts used for destructive distillation of coal is called *gas carbon*. In a similar manner petroleum coke is deposited on the walls of the retort used for distillation of crude petroleum.

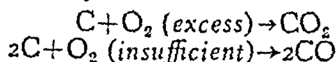
Both are good conductors of electricity when pressed into sticks and are used for making electrodes.

13. **Sugar charcoal.**—When sugar is heated strongly out of contact with air, sugar charcoal is obtained. It is the purest form of carbon.

14. Chemical Properties of Carbon.

(1) **Burning.** Any of the allotropic forms of carbon burns to give carbon dioxide when heated strongly in a free supply of air or oxygen while carbon monoxide is obtained in an insufficient supply of air or oxygen.

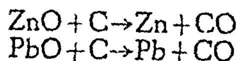
This is the **proof of the chemical identity** *of the various allotropic forms of carbon.*



$$C + O_2\ (excess) \rightarrow CO_2$$
$$2C + O_2\ (insufficient) \rightarrow 2CO$$

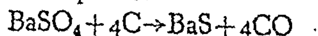
(2) **Reducing properties.** Due to the ease with which it burns to give monoxide or dioxide, it acts as a strong reducing agent. For example, it reduces

(*i*) Metallic oxides to metals.



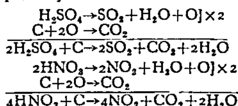
$$ZnO + C \rightarrow Zn + CO$$
$$PbO + C \rightarrow Pb + CO$$

(*ii*) Sulphates to sulphides.



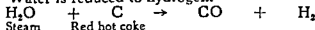
$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

(*iii*) Sulphuric acid and nitric acid to sulphur dioxide and nitrogen dioxide respectively.



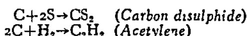
$$H_2SO_4 \rightarrow SO_2 + H_2O + O] \times 2$$
$$C + 2O \rightarrow CO_2$$
$$\overline{2H_2SO_4 + C \rightarrow 2SO_2 + CO_2 + 2H_2O}$$
$$2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 2$$
$$C + 2O \rightarrow CO_2$$
$$\overline{4HNO_3 + C \rightarrow 4NO_2 + CO_2 + 2H_2O}$$

(*iv*) Water is reduced to hydrogen.



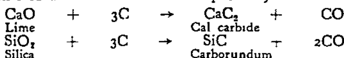
$$\underset{\text{Steam}}{H_2O} + \underset{\text{Red hot coke}}{C} \rightarrow CO + H_2$$

(3) **Combination with elements.** It combines with sulphur when vapours of sulphur are passed over red hot carbon to give carbon disulphide. With hydrogen it combines when electric arc is struck between carbon electrodes in an atmosphere of hydrogen, to give acetylene.



$$C + 2S \rightarrow CS_2 \quad (\textit{Carbon disulphide})$$
$$2C + H_2 \rightarrow C_2H_2 \quad (\textit{Acetylene})$$

(4) **Formation of Calcium carbide and Carborundum.** On heating with lime and silica in an electric furnace, carbon gives calcium carbide and carborundum respectively.



$$\underset{\text{Lime}}{CaO} + 3C \rightarrow \underset{\text{Cal carbide}}{CaC_2} + CO$$
$$\underset{\text{Silica}}{SiO_2} + 3C \rightarrow \underset{\text{Carborundum}}{SiC} + 2CO$$

15. **Position of Carbon in the Periodic Table.**—Carbon is placed at the top of the sub-group IVA of the Periodic Table, the other elements being silicon, germanium, tin and lead. There exists a regular gradation in their properties as given below :

(i) There are four electrons in the outermost orbit of each one of the elements which are, therefore, tetravalent elements.

[illegible] sively with the rise of [illegible] non-metals whereas [illegible]

(*iii*) All of them give acidic oxides of the formula MO_2.

(*iv*) Their affinity for hydrogen also decreases with atomic weight progressively. Hydrides of carbon are most stable, those of silicon are less stable and those of the remaining elements unstable.

TEST YOURSELF ON THESE REACTIONS

Write equations for reactions, if any, between .

1. Coke+Sand (heated in an electric furnace).

2. Carbon+(*i*) Zinc oxide, (*ii*) Lead oxide, (*iii*) Barium sulphate, (*iv*) Sulphuric acid, (*v*) Nitric acid, (*vi*) Steam, (*vii*) Sulphur, (*viii*) Hydrogen, (*ix*) Lime, (*x*) Burning.

(*ii*) On burning it gives bone-ash which is calcium phosphate chemically. Bone-ash is used for the manufacture of phosphorus and phosphoric acid.

10. **Lampblack.**—It is manufactured by burning oils (rich in carbon) in an insufficient supply of air and depositing the soot on wet blankets hung in a room.

It is a velvety black powder used in the manufacture of Indian ink, printer's ink, black paints and varnishes and carbon papers.

11. **Carbon black.**—It is prepared by burning natural gas in limited supply of air and differs from lampblack in being not so greasy. Soot from the burning gas is deposited on the underside of a revolving disc and then scraped off and stored in bags.

It is added to the rubber mix used for making automobile tyres, and has replaced lampblack used for a number of purposes.

12. **Gas carbon and Petroleum coke.**—Carbon scraped from the walls of the retorts used for destructive distillation of coal is called *gas carbon*. In a similar manner petroleum coke is deposited on the walls of the retort used for distillation of crude petroleum.

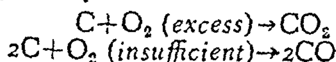
Both are good conductors of electricity when pressed into sticks and are used for making electrodes.

13. **Sugar charcoal.**—When sugar is heated strongly out of contact with air, sugar charcoal is obtained. It is the purest form of carbon.

14. Chemical Properties of Carbon.

(1) **Burning.** Any of the allotropic forms of carbon burns to give carbon dioxide when heated strongly in a free supply of air or oxygen while carbon monoxide is obtained in an insufficient supply of air or oxygen.

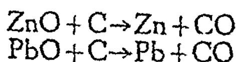
This is the **proof of the chemical identity** *of the various allotropic forms of carbon.*



$$C + O_2 \text{ (excess)} \rightarrow CO_2$$
$$2C + O_2 \text{ (insufficient)} \rightarrow 2CO$$

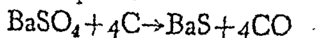
(2) **Reducing properties.** Due to the ease with which it burns to give monoxide or dioxide, it acts as a strong reducing agent. For example, it reduces

(*i*) Metallic oxides to metals.



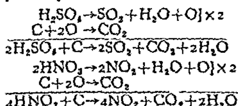
$$ZnO + C \rightarrow Zn + CO$$
$$PbO + C \rightarrow Pb + CO$$

(*ii*) Sulphates to sulphides.



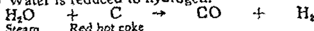
$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

(iii) Sulphuric acid and nitric acid to sulphur dioxide and nitrogen dioxide respectively.



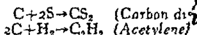
$$H_2SO_4 \rightarrow SO_2 + H_2O + O] \times 2$$
$$C + 2O \rightarrow CO_2$$
$$2H_2SO_4 + C \rightarrow 2SO_2 + CO_2 + 2H_2O$$
$$2HNO_3 \rightarrow 2NO_2 + H_2O + O] \times 2$$
$$C + 2O \rightarrow CO_2$$
$$4HNO_3 + C \rightarrow 4NO_2 + CO_2 + 2H_2O$$

(iv) Water is reduced to hydrogen.



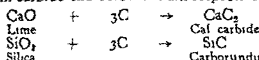
$$\underset{\text{Steam}}{H_2O} + \underset{\text{Red hot coke}}{C} \rightarrow CO + H_2$$

(3) **Combination with *elements*.** *It combines* with sulphur ›hen vapours of sulphur are passed over red hot carbon to give arbon disulphide. With hydrogen it combines when electric arc : struck between carbon electrodes in an atmosphere of ... ɔ give acetylene.



$$C + 2S \rightarrow CS_2 \quad (\textit{Carbon di...})$$
$$2C + H_2 \rightarrow C_2H_2 \quad (\textit{Acetylene})$$

(4) **Formation of Calcium carbide and Car...**)n heating with lime and silica in an electric furn... ives calcium carbide and carborundum respectively.



$$\underset{\text{Lime}}{CaO} + 3C \rightarrow \underset{\text{Cal carbide}}{CaC_2} + ...$$
$$\underset{\text{Silica}}{SiO_2} + 3C \rightarrow \underset{\text{Carborundu...}}{SiC}$$

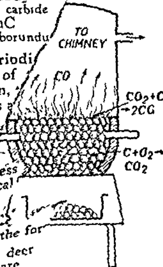
15. Position of Carbon in the Periodi... ; placed at the top of the sub-group IVA of ... he other elements being silicon, germanium, ... xists a regular gradation in their properties ...

(i) There are four electrons in the o... ne of the elements which are, therefore, t...

(ii) Metallic character increases progress... tomic weight. First two of them are typical... he last two are definitely metals.

(iii) All of them give acidic oxides ... of the for...

(iv) Their affinity for hydrogen ... also decr... ›eight progressively. Hydrides of c... arbon are ıf silicon are less stable and tho... se of the ... ınstable.



...1—Formation of carbon ...noxide by reduction of carbon dioxide.

TEST YOURSELF ON THESE

...re specimen of carbon ...

A mixture of oxalic acid and concentrated sulphuric acid is heated in a round-bottom flask (Fig. 47·2) and the mixture of

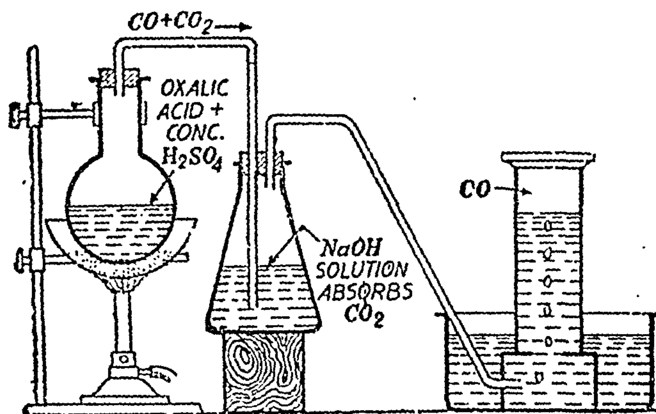


Fig. 47·2—Preparation of carbon monoxide in the laboratory.

carbon monoxide and carbon dioxide evolved as a result of dehydration of oxalic acid by concentrated sulphuric acid, is passed through a wash bottle containing caustic soda, NaOH solution which absorbs carbon dioxide. Carbon monoxide freed from carbon dioxide is collected over water.

(*ii*) Carbon monoxide can also be conveniently prepared in the laboratory by dehydration of formic acid with concentrated sulphuric acid.



$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Conc.}}{H_2SO_4} \rightarrow CO + \underset{\text{Sulphuric acid hydrate}}{[H_2SO_4 + H_2O]}$$

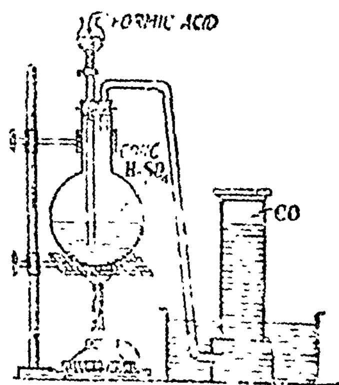
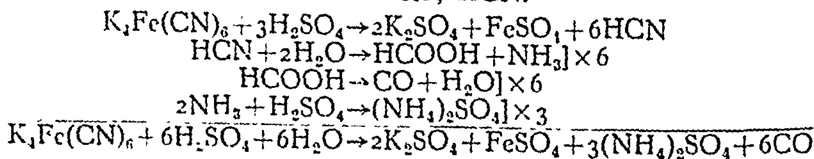


Fig. 47·3—Laboratory preparation of carbon monoxide.

Concentrated sulphuric acid is taken in a round-bottom flask and formic acid dropped in it from a dropping funnel (Fig. 47·3). The flask is heated when carbon monoxide is liberated and collected over water.

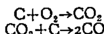
Caution. *Experiment should be performed in a fume cupboard as the gas is highly poisonous and should never be inhaled.*

(2) By heating potassium ferrocyanide with concentrated sulphuric acid. Dilute sulphuric acid should not be used as it gives hydrocyanic acid, HCN.



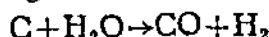
$$K_4Fe(CN)_6 + 3H_2SO_4 \rightarrow 2K_2SO_4 + FeSO_4 + 6HCN$$
$$HCN + 2H_2O \rightarrow HCOOH + NH_3] \times 6$$
$$HCOOH \rightarrow CO + H_2O] \times 6$$
$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4] \times 3$$
$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Manufacture. (*i*) A mixture of carbon monoxide and nitrogen (*Producer gas*) is obtained by blowing air through a bed of red hot coke (Fig. 47·2). Carbon dioxide produced in the lower part is reduced to carbon monoxide.



$$C+O_2 \rightarrow CO_2$$
$$CO_2+C \rightarrow 2CO$$

(*ii*) A mixture of carbon monoxide and hydrogen (*Water gas*) is obtained by blowing steam over red hot coke (Fig. 48·1).



$$C+H_2O \rightarrow CO+H_2$$

3. Properties of Carbon monoxide.

(*a*) Physical. (*i*) It is a colourless, tasteless gas with a faint odour.

(*ii*) It is very sparingly soluble in water and is almost as heavy as air (vapour density=14, that of air being 14·4).

(*iii*) It condenses to a liquid (b.p. −190°C) when cooled under pressure.

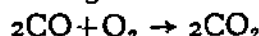
(*iv*) It is extremely poisonous in nature. A concentration of one in 800 volumes of air will produce death in 30 minutes.

It combines with Haemoglobin (red colouring matter) of the blood t
thus rende
gas is a tre
ness, then
closed rooms with charcoal-fire burning inside have died in large numbers due to carbon monoxide poisoning.

b
g

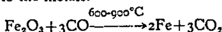
(*b*) Chemical. (1) It is neutral towards litmus and is not decomposed by heat.

(2) Burning. It is non-supporter of combustion but burns in air with a blue flame to give carbon dioxide.



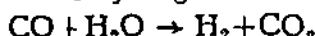
$$2CO+O_2 \rightarrow 2CO_2$$

(3) Reducing Property. Due to the ease with which it is oxidised ($2CO+O_2 \rightarrow 2CO_2$), it acts as a reducing agent. For example, metallic oxides when heated in current of carbon monoxide are reduced to the metals.



$$Fe_2O_3+3CO \xrightarrow{600\text{-}900^\circ C} 2Fe+3CO_2$$

At high temperature and pressure and in the presence of a catalyst it reduces steam to hydrogen.



$$CO+H_2O \rightarrow H_2+CO_2$$

(4) Unsaturated Nature. All the four valencies of carbon are not satisfied in carbon monoxide. It is however an unsaturated

A mixture of oxalic acid and concentrated sulphuric acid is heated in a round-bottom flask (Fig. 47·2) and the mixture of

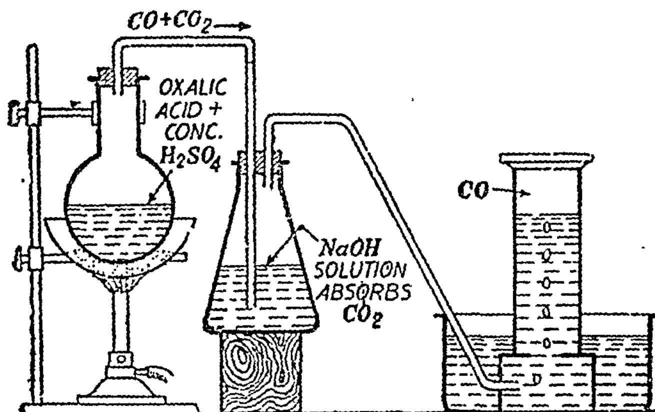


Fig. 47·2—Preparation of carbon monoxide in the laboratory.

carbon monoxide and carbon dioxide evolved as a result of dehydration of oxalic acid by concentrated sulphuric acid, is passed through a wash bottle containing caustic soda, NaOH solution which absorbs carbon dioxide. Carbon monoxide freed from carbon dioxide is collected over water.

(*ii*) Carbon monoxide can also be conveniently prepared in the laboratory by dehydration of formic acid with concentrated sulphuric acid.



$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Conc.}}{H_2SO_4} \rightarrow CO + \underset{\text{Sulphuric acid hydrate}}{[H_2SO_4+H_2O]}$$

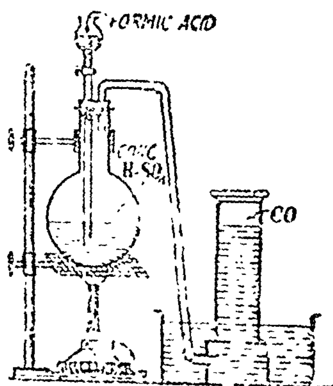
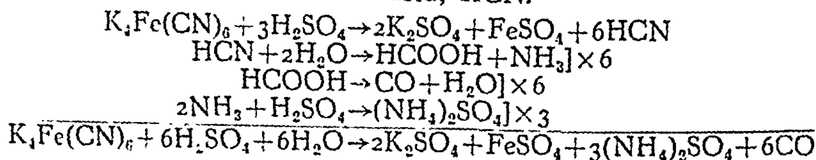


Fig. 47·3—Laboratory preparation of carbon monoxide.

Concentrated sulphuric acid is taken in a round-bottom flask and formic acid dropped in it from a dropping funnel (Fig. 47·3). The flask is heated when carbon monoxide is liberated and collected over water.

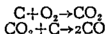
Caution. *Experiment should be performed in a fume cupboard as the gas is highly poisonous and should never be inhaled.*

(2) By heating potassium ferrocyanide with concentrated sulphuric acid. Dilute sulphuric acid should not be used as it gives hydrocyanic acid, HCN.



$$K_4Fe(CN)_6 + 3H_2SO_4 \rightarrow 2K_2SO_4 + FeSO_4 + 6HCN$$
$$HCN + 2H_2O \rightarrow HCOOH + NH_3] \times 6$$
$$HCOOH \rightarrow CO + H_2O] \times 6$$
$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4] \times 3$$
$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

Manufacture. (*i*) A mixture of carbon monoxide and nitrogen (*Producer gas*) is obtained by blowing air through a bed of red hot coke (Fig. 47·2). Carbon dioxide produced in the lower part is reduced to carbon monoxide.



$$C+O_2 \rightarrow CO_2$$
$$CO_2+C \rightarrow 2CO$$

(*ii*) A mixture of carbon monoxide and hydrogen (*Water gas*) is obtained by blowing steam over red hot coke (Fig. 48·1).



$$C+H_2O \rightarrow CO+H_2$$

3. Properties of Carbon monoxide.

(*a*) **Physical.** (*i*) It is a colourless, tasteless gas with a faint odour.

(*ii*) It is very sparingly soluble in water and is almost as heavy as air (vapour density=14, that of air being 14·4).

(*iii*) It condenses to a liquid (b.p. −190°C) when cooled under pressure.

(*iv*) It is extremely poisonous in nature. A concentration of one in 800 volumes of air will produce death in 30 minutes.

It combines with Haemoglobin (red colouring matter) of the blood to give carboxy haemoglobin, a cherry-red compound and thus renders it useless as an oxygen carrier. Being odourless, the gas is
ness,
closec
numbers due to carbon monoxide poisoning.

A victim of c
be brought in the c
gen—a mixture of

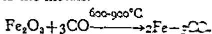
(*b*) **Chemical.** (1) It is neutral towards litmus
decomposed by heat.

(2) **Burning.** It is non-supporter of combustion
in air with a blue flame to give carbon dioxide.



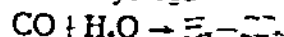
$$2CO+O_2 \rightarrow 2CO_2$$

(3) **Reducing Property.** Due to the ease
oxidised ($2CO+O_2 \rightarrow 2CO_2$), it acts as a red
ple, metallic oxides when heated in current
are reduced to the metals.



$$Fe_2O_3+3CO \xrightarrow{600\text{-}900°C} 2Fe+$$

At high temperature and pres
catalyst it reduces steam to hydro

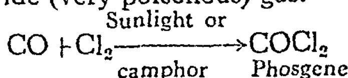


$$CO+H_2O \rightarrow$$

(4) **Unsaturated Nature.**
are not satisfied in carbon

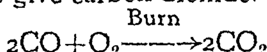
compound and gives addition products with a number of substances.

(*i*) **With Chlorine.** Carbon monoxide combines with chlorine in the presence of sunlight or camphor to give phosgene or carbonyl chloride (very poisonous) gas.



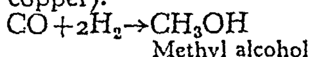
$$CO + Cl_2 \xrightarrow[\text{camphor}]{\text{Sunlight or}} \underset{\text{Phosgene}}{COCl_2}$$

(*ii*) **With Oxygen.** With oxygen carbon monoxide combines when burnt to give carbon dioxide.



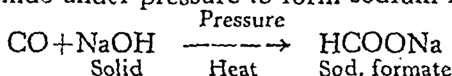
$$2CO + O_2 \xrightarrow{\text{Burn}} 2CO_2$$

(*iii*) **With Hydrogen.** Carbon monoxide combines with hydrogen when heated to 150—400°C in the presence of a catalyst (ZnO + finely divided copper).



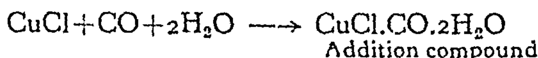
$$CO + 2H_2 \rightarrow \underset{\text{Methyl alcohol}}{CH_3OH}$$

(*iv*) **With Sodium hydroxide.** Solid caustic soda absorbs carbon monoxide under pressure to form sodium formate.



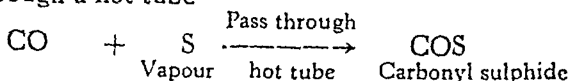
$$CO + \underset{\text{Solid}}{NaOH} \xrightarrow[\text{Heat}]{\text{Pressure}} \underset{\text{Sod. formate}}{HCOONa}$$

(*v*) **With Cuprous chloride.** An ammoniacal solution of cuprous chloride absorbs carbon monoxide to produce an addition compound.



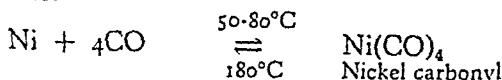
$$CuCl + CO + 2H_2O \longrightarrow \underset{\text{Addition compound}}{CuCl.CO.2H_2O}$$

(*vi*) **With Sulphur.** Carbon monoxide and sulphur vapour combine to form carbonyl sulphide, COS when their mixture is passed through a hot tube



$$CO + \underset{\text{Vapour}}{S} \xrightarrow[\text{hot tube}]{\text{Pass through}} \underset{\text{Carbonyl sulphide}}{COS}$$

(*vii*) **With Nickel.** On passing carbon monoxide over heated nickel at 50—80°C, it gives volatile nickel carbonyl, $Ni(CO)_4$ which decomposes again at a higher temperature to give nickel and carbon monoxide.



$$Ni + 4CO \underset{180°C}{\overset{50\text{-}80°C}{\rightleftharpoons}} \underset{\text{Nickel carbonyl}}{Ni(CO)_4}$$

4. **Uses of Carbon monoxide.**—(*i*) In the form of producer gas or water gas it is used as fuel and for other technical purposes.

(*ii*) In the metallurgy of nickel.

(*iii*) In the manufacture of methanol and synthetic petrol.

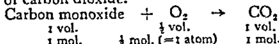
(*iv*) In the manufacture of phosgene used in dye industry and warfare.

(*v*) In metallurgy as a reducing agent.

5. **Tests.**—(*i*) It burns with a blue flame.

(*ii*) A filter paper soaked in platinum or palladium chloride is turned pink, green or black due to reduction of the chloride by carbon monoxide.

6. **Formula of Carbon monoxide.**—A known volume of carbon monoxide is sparked with a known volume of oxygen (*excess*) in a eudiometer and the volume of carbon dioxide formed and oxygen left is determined. It is found that one volume of carbon monoxide combines with half a volume of oxygen to form one volume of carbon dioxide.



Carbon monoxide	+ O_2	→ CO_2
1 vol.	½ vol.	1 vol.
1 mol.	½ mol. (=1 atom)	1 mol.

... conclude that one ... lecule (=1 atom) ... CO_2.

Its formula must, therefore, be CO. This is further confirmed by its vapour density (=14).

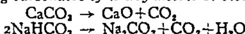
CARBON DIOXIDE, CO_2

7. Historical.—Carbon dioxide has been known since very early times. Black (1755) showed that it was a constituent of carbonates and named it "fixed air". It was Lavoisier who proved that it was an oxide of carbon.

8. **Occurrence.**—Carbon dioxide is present in air to the extent of about 0·03 per cent by volume. It accumulates in caves, mines or dry wells near lime kilns. It is evolved from volcanoes, *e.g.*, Valley of Death in Jawa is strewn with skeletons of human beings, animals and birds who died there because of oxygen starvation. It is a product of combustion, respiration and fermentation reactions.

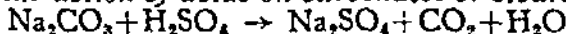
9. **Preparation.**—Carbon dioxide is produced when carbon or its compounds burn in an excess of air. It cannot, however, be conveniently prepared by this method. It can be prepared :

(i) *By heating carbonates of heavy metals or bicarbonates.*



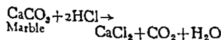
$$CaCO_3 \rightarrow CaO + CO_2$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

(ii) *By the action of acids on carbonates or bicarbonates.*



$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + H_2O$$

(iii) **Laboratory Preparation.** Carbon dioxide is prepared ... dilute hydrochloric acid on mar- ... funnel, when carbon dioxide is evolved and collected by an upward displacement of air (Fig. 47·4).



$$\underset{\text{Marble}}{CaCO_3} + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

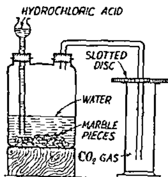
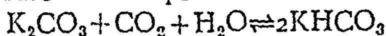


Fig 47·4—Laboratory preparation of carbon dioxide

10. **Manufacture.** — (*i*) **From Flue Gases.** Large amounts of carbon dioxide are manufactured from flue gases (waste products of combustion). These are passed under pressure

into scrubbers containing potassium carbonate which is converted to potassium bicarbonate. Carbon dioxide is again set free by releasing the pressure and compressed into steel cylinders.



$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3$$

(*ii*) **From Limestone.** Large quantities of carbon dioxide are obtained as by-products during the manufacture of lime by burning limestone in lime kilns.



$$\underset{\text{Limestone}}{CaCO_3} \rightarrow \underset{\text{Lime}}{CaO} + CO_2$$

(*iii*) **By Fermentation.** During the manufacture of alcohol by fermentation of sugar, carbon dioxide is obtained as a by-product.



$$\underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow \underset{\text{Alcohol}}{2C_2H_5OH} + \underset{\text{By-product}}{2CO_2}$$

11. Properties of Carbon dioxide.

(*a*) **Physical.** (*i*) It is a colourless gas with a faint smell

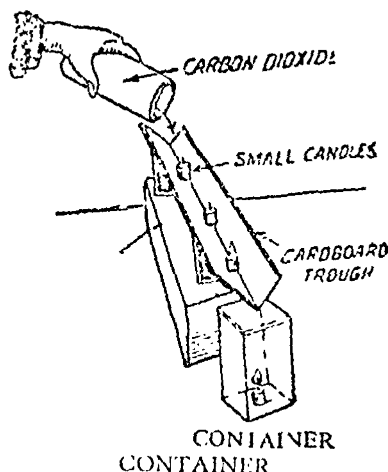


Fig. 47·5 Carbon dioxide can be poured like water.

(*ii*) It is about 1·5 times heavy as air and can be pou like water.

Expt. 1. Arrange a pa trough in an inclined position. Li a few small candles in the trough the container below (Fig. 47·5). P carbon dioxide from gas jar down inclined trough. As it flows downw the candles are extinguished one a another.

(*iii*) It is not fairly solul in water. Aerated wa a so tion of carbon dioxi under pressure.

(*iv*) It is not po animals die in it fo oxygen.

(*v*) It can b under pressure (50—60 atmospheres) and solidified.

Expt. 2. Hold a woollen bag at the mouth of a carbon dioxide cylinder and open the valve (Fig. 47·6). Liquid carbon dioxide vaporizes suddenly due to the sudden release of pressure. Cooling, caused by evaporation, solidifies a part of carbon dioxide and we get carbon dioxide snow or dry ice.

Caution. *Solid carbon dioxide should be gently handled as it produces burns when pressed against the skin.*

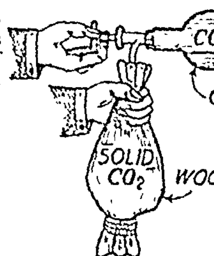
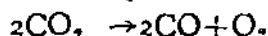


Fig. 47·6.—Prepa

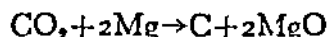
(*b*) Chemical.

(i) Stability. It is fairly stable. For example, only about 0·32 per cent of the gas is decomposed when heated to 1500°C.



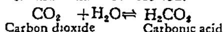
$$2CO_2 \rightarrow 2CO + O_2$$

(ii) Incombustible and Non-supporter of Combustion. Ordinarily carbon dioxide is neither combustible nor a supporter *of combustion. However, certain very active metals, e g., magnesium*, sodium and potassium continue burning in a jar of the gas.



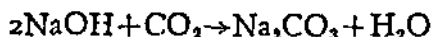
$$CO_2 + 2Mg \rightarrow C + 2MgO$$

(iii) Acidic Nature. It dissolves in water to give carbonic acid and is, therefore, called *carbonic anhydride*. The acid is, however, unstable and cannot be isolated.

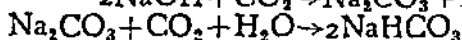


$$\underset{\text{Carbon dioxide}}{CO_2} + H_2O \rightleftharpoons \underset{\text{Carbonic acid}}{H_2CO_3}$$

It turns moist blue litmus slightly reddish and neutralizes alkalis to give two series of salts, carbonates and bicarbonates.

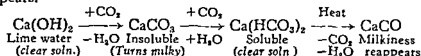


$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$



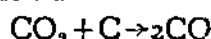
$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

(iv) Action on lime water. When bubbled through lime water it first turns milky and is again clear after some time when more gas is bubbled. On boiling the clear solution, milkiness reappears.



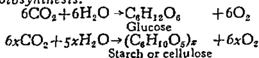
$$\underset{\substack{\text{Lime water}\\ \textit{(clear soln.)}}}{Ca(OH)_2} \xrightarrow[-H_2O]{+CO_2} \underset{\substack{\text{Insoluble}\\ \textit{(Turns milky)}}}{CaCO_3} \xrightarrow[+H_2O]{+CO_2} \underset{\substack{\text{Soluble}\\ \textit{(clear soln.)}}}{Ca(HCO_3)_2} \xrightarrow[-CO_2,\ -H_2O]{\text{Heat}} \underset{\substack{\text{Milkiness}\\ \text{reappears}}}{CaCO}$$

(*v*) Reduction When passed through red hot coke, it is reduced to carbon monoxide.



$$CO_2 + C \rightarrow 2CO$$

(*vi*) Photosynthesis. Carbon dioxide is absorbed by plants in the presence of chlorophyll (green colouring matter in leaves) and sunlight to produce glucose, starch and cellulose. The process is known as *photosynthesis*.



$$6CO_2 + 6H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

$$6xCO_2 + 5xH_2O \rightarrow \underset{\text{Starch or cellulose}}{(C_6H_{10}O_5)_x} + 6xO_2$$

12. Tests.—(i) A burning candle is put out but burning magnesium continues burning in the gas jar.

(*ii*) It turns lime water milky.

13. Uses.—(i) *In household fire extinguishers* Air containing about 15 per cent of carbon dioxide does not support combustion. Carbon dioxide is, therefore, used for extinguishing fire.

(*a*) Dry powder extinguishers contain sand and baking soda ($NaHCO_3$) which is thrown over the burning fire where it is decomposed by heat and carbon dioxide is liberated.



$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

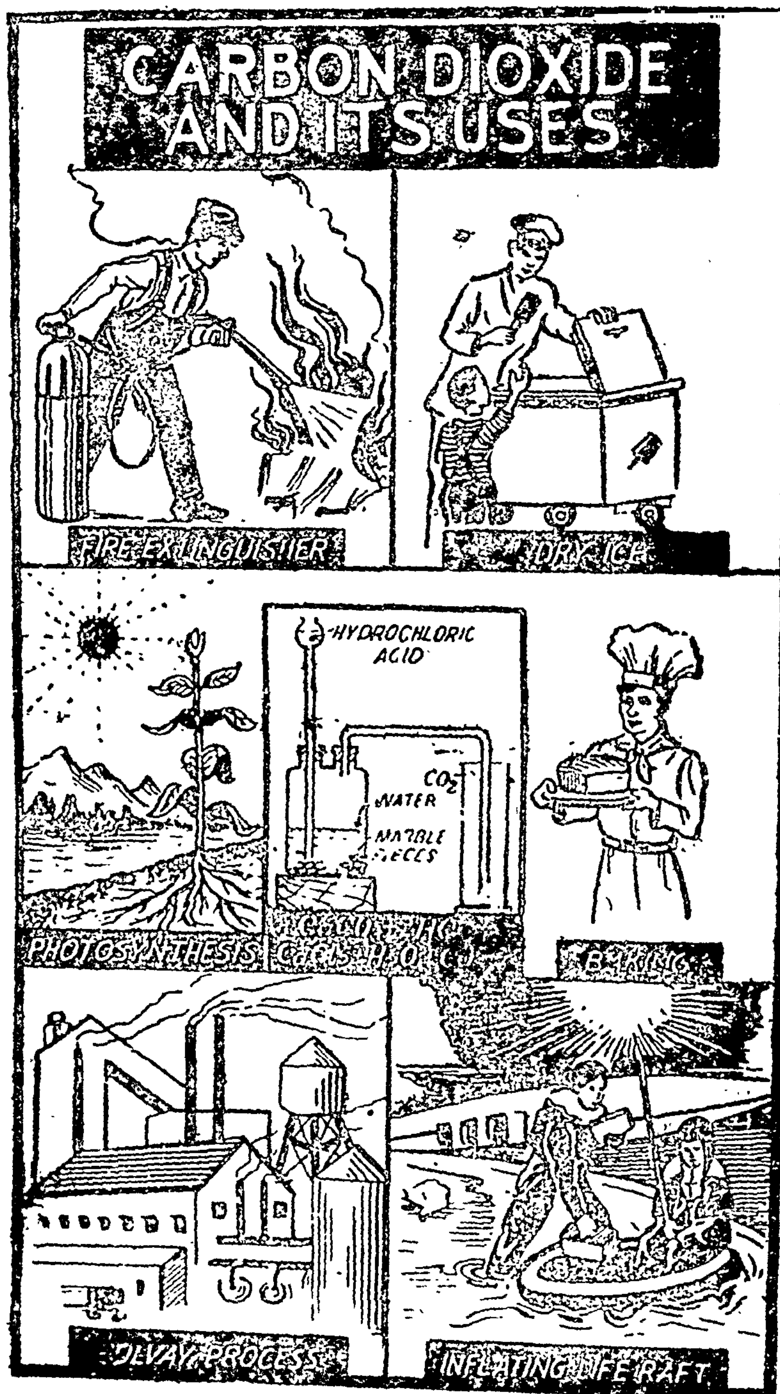
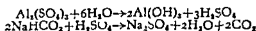

CARBON DIOXIDE
AND ITS USES
FIRE EXTINGUISHER
DRY ICE
HYDROCHLORIC
ACID
CO_2
WATER
PHOTOSYNTHESIS
INFLATING LIFE RAFT

Fig. 47'7.

(c) In foamite fire-extinguishers sulphuric



$$Al_2(SO_4)_3+6H_2O \rightarrow 2Al(OH)_3+3H_2SO_4$$
$$2NaHCO_3+H_2SO_4 \rightarrow Na_2SO_4+2H_2O+2CO_2$$

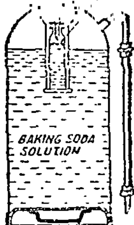


Fig. 47·8—Baking soda, sulphuric acid type fire-extinguisher.

The foam surrounds the burning object and cuts off supply of air. It has proved very effective in extinguishing oil fires which spread instead of being extinguished by water (Fig. 47·9).

(ii) In the manufacture of aerated water.

(iii) Dry ice is used for refrigeration (e.g., for handling fish and ice-cream) and in the treatment of local sore.

(iv) In the manufacture of white lead and baking soda (Solvay Process).

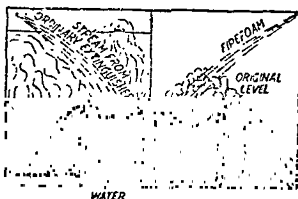


Fig. 47·9 (a)—Oil overflows the container as water is poured into it and thus results in spreading the fire.

Fig. 47·9 (b)—Foam surrounds the burning oil, cuts off air and thus extinguishes the fire.

(v) Carbogen, a mixture of oxygen with 5—10 per cent carbon dioxide, is given to pneumonia patients and victims of carbon monoxide poisoning for artificial respiration. Carbon dioxide present stimulates breathing.

14. **Carbon dioxide-Oxygen cycle in Nature.**—Large quantities of carbon dioxide are being constantly produced as a result of combustion and fermentation of plants and plant products.

Animals also breathe in oxygen present in air and exhale carbon dioxide (*Respiration*). Decay of animals after death gives carbon dioxide. In spite of all this percentages of carbon dioxide and oxygen remain practically constant in air. This is due to a never-ending *carbon dioxide-oxygen cycle* in nature. During the day time plants take up carbon dioxide from air and return oxygen (*photosynthesis*, *see* page 2·239). At night the plants take in oxygen and give out carbon dioxide like animals but the carbon dioxide added is only a very small fraction of the carbon dioxide removed by them by photosynthesis. These opposing operations constitute the carbon dioxide-oxygen cycle and keep the percentage of carbon dioxide in air fairly constant.

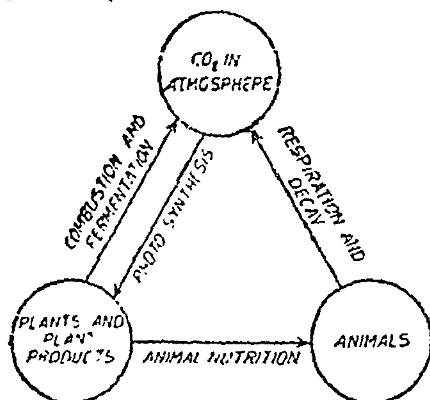


Fig. 47·10—Carbon dioxide-Oxygen cycle in nature.

15 **Formula of Carbon Dioxide.**—The apparatus used consists of a U-tube with a bulb in one of the limbs (Fig. 47·11). Two platinum wires are sealed in the bulb and carry a spoon *A* at their lower end.

Some oxygen is enclosed in the bulb and its volume noted after equalizing the mercury level in the two limbs of the U-tube. A small piece of carbon is placed in the spoon and heated by passing electric current through platinum wires. Carbon burns away forming carbon dioxide but no change in volume is noticed on cooling showing that one volume of oxygen combines with carbon to give one volume of carbon dioxide.

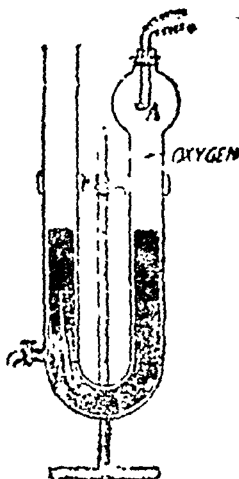


Fig. 47·11—Formula of carbon dioxide.

Applying Avogadro's law, we infer that one molecule (2 atoms) of oxygen combines with carbon (say, x atoms) to give one molecule of carbon dioxide. *i.e.*, its formula is C_xO_2 having molecular weight$=12x+32$.

Molecular weight of carbon dioxide as calculated from its vapour density ($=22$) data is found to be 44. Equating the two molecular weights, we have

$$12x+32=44 \qquad \text{whence } x=1$$

Hence Molecular formula of carbon dioxide is CO_2.

16. Carbonates and Bicarbonates.— Carbonic acid is a dibasic acid and gives rise to two series of salts, *carbonates* (normal salts) and *bicarbonates* (acid salts). These are prepared --

(i) By passing carbon dioxide through an alkali. The carbonate first formed changes to bicarbonate with excess of carbon dioxide.

$$2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O$$
$$Na_2CO_3+H_2O+CO_2 \rightarrow 2NaHCO_3$$

(*ii*) *By precipitation*. Heavy metal carbonates are precipitated from the salt solution with washing soda.

$$BaCl_2+Na_2CO_3 \rightarrow BaCO_3 \downarrow +2NaCl$$

General Properties. (*i*) *Solubility*. Carbonates are usually insoluble, only exceptions being alkali metal carbonates which are soluble in water. Alkali metal bicarbonates are soluble in water, those of other metals exist only in solution.

(*ii*) *Action of Heat*. Bicarbonates and non-alkali carbonates are decomposed by heat giving carbon dioxide.

$$2NaHCO_3 \rightarrow Na_2CO_3+CO_2+H_2O$$
$$CaCO_3 \rightarrow CaO+CO_2$$

(*iii*) *Action of Acids*. These are decomposed by acids with effervescence due to brisk evolution of carbon dioxide.

$$CaCO_3+2HCl \rightarrow CaCl_2+CO_2 \uparrow +H_2O$$
$$NaHCO_3+HCl \rightarrow NaCl+CO_2 \uparrow +H_2O$$

(*iv*) *With Magnesia mixture*. Soluble carbonates give a white precipitate of magnesium carbonate in cold whereas bicarbonates give a white precipitate on heating only.

$$Na_2CO_3+MgCl_2 \rightarrow \underset{\text{White ppt.}}{MgCO_3} + 2NaCl$$

$$NaHCO_3 \xrightarrow{MgCl_2} \underset{\text{Soluble}}{Mg(HCO_3)_2} \xrightarrow[-CO_2\,;\,-H_2O]{\text{Heat}} \underset{\text{White ppt.}}{MgCO_3}$$

(*v*) *Hydrolysis*. Being salts of weak acids, they undergo hydrolysis. The solutions behave alkaline. A carbonate solution gives a pink colour with phenolphthalein but a bicarbonate solution gives none.

Distinguishing Tests between Carbonates and Bicarbonates

Tests	Carbonates	Bicarbonates
1. Heat in dry test tube.	Carbonates of heavy metals give CO_2.	All bicarbonates give CO_2.
2. Treat with dil. HCl.	CO_2 evolved with effervescence, which turns lime water milky.	Same.
3. Solubility.	Only carbonates of alkali metals are soluble.	All bicarbonates are soluble.
4. To the solution add $MgSO_4$ soln.	Soluble carbonates give a ppt. in cold.	Give a ppt. only on heating.
5 To the soln. add phenolphthalein.	Pink colour.	No colour.

CARBON DISULPHIDE, CS_2

17. Manufacture.—Carbon disulphide is manufactured by passing vapours of sulphur over red hot coke. Carbon and sulphur unite to give carbon disulphide.

$$C+2S \rightarrow CS_2$$

In the Zahn's process for manufacturing carbon disulphide, molten sulphur is heated in a pre-heater. The vapours of sulphur pass into the adjoining retort packed with heated charcoal at 900°C (Fig. 47·12). Carbon disulphide vapours thus produced are condensed and purified by fractional distillation.

In Taylor's electric process a cylindrical furnace is used. It is 40 feet high and 16 feet in diameter and is packed with coke. Separate hoppers are provided for adding fresh coke and sulphur. Heating is done with the help of

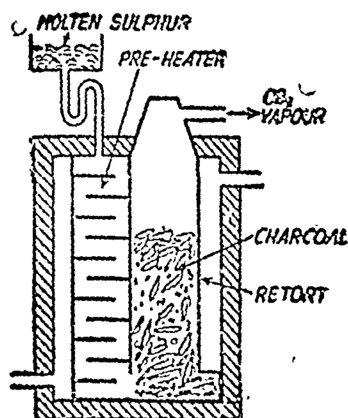


Fig. 47·12—Zahn's process.

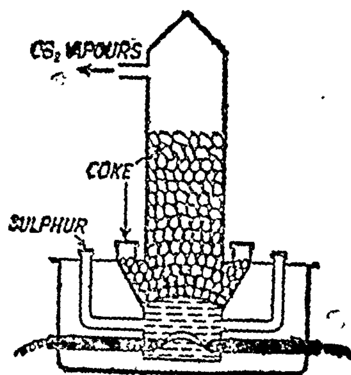


Fig. 47·13—Taylor's furnace.

an electric arc struck between two carbon electrodes (Fig. 47·13). Sulphur is vaporised in the lower part and vapours of sulphur pass through red hot coke to form carbon disulphide.

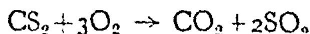
Vapours of carbon disulphide are let off through an exit near the top and condensed.

18. **Properties of Carbon Disulphide.**—(*i*) The commercial product is an almost colourless liquid (b.p. 46°C) with a disagreeable odour. The vapours are injurious to health.

(*ii*) It is heavier than water (its sp. gr. being 1·29) and is immiscible with it. With alcohol, ether and benzene, it mixes in all proportions.

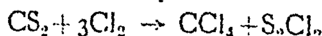
(*iii*) It is an excellent solvent for rubber, phosphorus, waxes, resins, oils and fats.

(*iv*) Its ignition temperature being very low, it is inflammable and burns rapidly with a blue flame. The vapours form an explosive mixture with air.



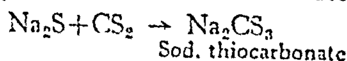
$$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$$

(*v*) With chlorine it reacts under suitable conditions to form carbon tetrachloride and sulphur chloride.



$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

(*vi*) With sulphides it forms thiocarbonates.



$$Na_2S + CS_2 \rightarrow \underset{\text{Sod. thiocarbonate}}{Na_2CS_3}$$

19. **Uses of Carbon Disulphide.**—(*i*) As a solvent in the manufacture of varnishes and matches. Rubber cement commonly used is a solution of rubber in carbon disulphide.

(*ii*) In one of the steps during the manufacture of viscose rayon.

(*iii*) In the manufacture of carbon tetrachloride.

(*iv*) For killing rats and mice, carbon disulphide is blown in their holes and ignited. Products of combustion settle down and *suffocate them.*

TEST YOURSELF ON THESE REACTIONS

Write equations for the chemical reactions, if any, between :

1. Hot. conc. sulphuric acid+(*i*) Oxalic acid, (*ii*) Formic acid, (*iii*) Potassium ferrocyanide.

2. Red hot coke+(*i*) Carbon dioxide, (*ii*) Steam.

3. Carbon monoxide+(*i*) Chlorine, (*ii*) Oxygen, (*iii*) Hydrogen, (*iv*) Solid caustic soda, (*v*) Cuprous chloride, (*vi*) Sulphur, (*vii*) Nickel.

4. Action of heat and acids on (*i*) Calcium carbonate, (*ii*) Sodium bicarbonate.

5. Carbon dioxide+(*i*) Burning magnesium, (*ii*) Water, (*iii*) Caustic soda, (*iv*) Lime water.

6. Carbon disulphide+(*i*) Chlorine, (*ii*) Sodium sulphite, (*iii*) Burning.

QUESTIONS

Essay-type Questions

1. Outline briefly the preparation of carbon monoxide in the laboratory. How has its formula been established ? Under what conditions does carbon monoxide react with : (*a*) Potassium hydroxide, (*b*) Chlorine, (*c*) Nickel, (*d*) Ferric oxide, (*e*) Oxygen, (*f*) Cuprous chloride, and (*g*) Hydrogen ? What products are formed in each case ? (*Bihar H S. 1966 ; M P. Board Inter 1965 ; Delhi H S. 1970, 69, 68 ; Punjab Pre-Univ. 1970*)

2. Give a convenient laboratory method for the preparation of a fairly [illegible] CO_2 assigned [illegible] equations to- [illegible] metal, (*c*) lime [illegible]

3. How will you distinguish between carbon monoxide and carbon dioxide ? How does nature manage to keep the balance of carbon dioxide in the atmosphere ? What uses can carbon dioxide be put to ? (*Bihar H S 1966, 61*)

4. (*a*) How would you remove small quantities of carbon monoxide from carbon dioxide ?

(*b*) How will you establish the composition of carbon monoxide ? (*M P Board Inter. 1965*)

(*c*) Write a short note on carbon dioxide-oxygen cycle. (*Punjab Pre-Univ 1971 ; Punjab H.S 1963 ; Bihar H S. 1964, 63 Supp*)

5. How will you prove that the formula of carbon dioxide is CO_2 ? How will you convert the two common oxides of carbon into each other ?

6. How is carbon disulphide manufactured ? Describe its important properties and uses.

7. Write a brief note on fire-extinguishers. (*Punjab H.S.* 1

8. Write a short note on Photosynthesis. (*Bihar H.S.* 1965, 62 Su

Test Your Understanding :

9. Fill in the blanks in the following :

(*a*) When potassium ferrocyanide is heated with conc. sulphuric acid is evolved.

(*b*) On heating oxalic acid and conc. sulphuric acid......is evolved.

(*c*) Carbon..... is a neutral oxide while......is an acidic oxide.

(*d*) Carbon monoxide reacts with Cl_2 in......to produce......

(*e*) Carbon dioxide can be obtained by the action of dilute acids on.

(*f*) When carbon dioxide is bubbled through lime water for a long t ..... is obtained.

KEY

9. (*a*) CO ;

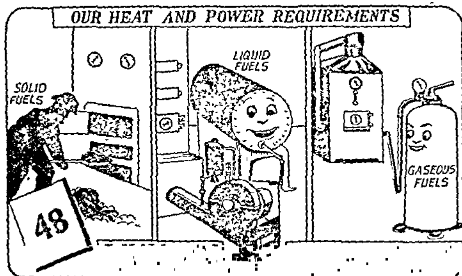
(*b*) a mixture of CO_2 and CO ;

(*c*) monoxide, carbon dioxide ;

(*d*) presence of sunlight, phosgene or carbonyl chloride ;

(*e*) carbonates and bicarbonates ;

(*f*) a clear solution containing calcium bicarbonate.



Fuel Gases

1. Fuel.—*Any combustible substance which may be burnt to supply heat energy without the production of excessively objectionable by-products is called a fuel*. Requisites of a good fuel are: (*i*) It should be cheap, (*ii*) should yield little ash, (*iii*) should have a high heat content, and (*iv*) should not give on burning any undesirable products. Different types of fuels that we come across are:

(*a*) *Solid fuels.* These include wood, coal, coke, charcoal, etc. These are derived from plants directly or indirectly.

(*b*) *Liquid fuels.* Petroleum products and alcohol are the examples of various liquid fuels used. These are more convenient and leave no solid ash.

(*c*) *Gaseous fuels.* Combustible gases make excellent fuels. These are most convenient to use.

2. Fuel Gases.—Gaseous fuels have all the advantages of liquid fuels. These can flow through pipes, can be lighted at a moment's notice, leave no ash and have high heat content. Fuel gases are, therefore, widely used for cooking and heating in homes as well as in industries. Important gases commonly used as fuel are:

(*i*) Water Gas, (*ii*) Producer Gas,
(*iii*) Semi-water Gas, (*iv*) Coal Gas,
(*v*) Oil Gas, and (*vi*) Natural Gas.

3. **Water Gas.**—A mixture of carbon monoxide and hydrogen obtained, when a blast of steam is forced up through a white hot bed of coke or coal, is commonly known as *water gas.*



$$\underset{\text{White hot steam}}{C + H_2O} \rightarrow \underset{\text{Water gas}}{(CO + H_2)} - 29{,}000 \text{ cal.}$$

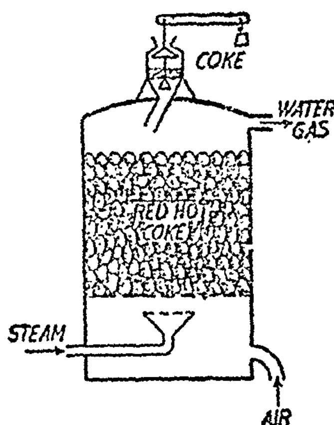
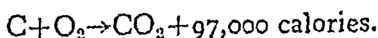


Fig. 48·1—Manufacture of water gas.

The reaction is endothermic and the blast of steam cools the glowing coke in a few minutes. The process has, therefore, to be interrupted and a blast of air is passed through the generator to raise the coke to the required temperature again.



$$C + O_2 \rightarrow CO_2 + 97{,}000 \text{ calories.}$$

A water gas generator (Fig. 48·1) is a tower packed with coke and provided with a hopper at the top for adding coke and two pipes near the bottom for blowing steam and air at will.

During the "steam run" (period when steam is blown in), water gas is produced. This is led out through an exit near the top and collected. During the "air run" (warming up process when air is blown in), the products of combustion (mainly nitrogen, carbon monoxide and carbon dioxide) are allowed to pass into the atmosphere. The manufacture of water gas is, therefore, an intermittent process.

Water gas contains 40—50 per cent of carbon monoxide, 45—50 per cent of hydrogen, 3—7 per cent of carbon dioxide and 4—5 per cent of nitrogen. To increase the fuel value of water gas, it is enriched by two methods.

(*i*) *By spraying fuel oil.* The gas is passed through the *carburetter*, a tower packed with chequer-work heated to white heat and a fuel oil is sprayed in. The molecules of the oil are broken up (cracked) into simpler molecules of very high fuel value. The mixture is next passed through a similar tower called superheater wherein cracking is completed and a uniform mixture is obtained.

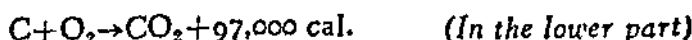
(*ii*) *By adding propane or butane* obtained as by-products in petroleum refining or from natural gas.

Uses.—Water gas finds use : (*i*) As a fuel gas.

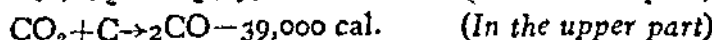
(*ii*) As a source of industrial hydrogen.

(*iii*) For lighting purposes with the help of Welsbach mantles (*see* page 2·257).

4 **Producer Gas.**—Producer gas which is essentially a mixture of carbon monoxide and nitrogen is prepared by burning coke, etc., in a limited supply of air. Carbon burns at the bottom
reduced to
of red hot
ogen (from
air) with traces of carbon dioxide and hydrocarbons comes out. These are led out through an exit near the top. The fuel value of the gas is not very high. It is used as a fuel on the spot while still hot.



$C+O_2 \rightarrow CO_2+97{,}000$ cal. *(In the lower part)*



$CO_2+C \rightarrow 2CO-39{,}000$ cal. *(In the upper part)*

5 Gas Producer.—Plant used for the manufacture of pro- . It is a cylindrical furnace

the hopper at the top and a blast of air is blown in through a pipe at the bottom.

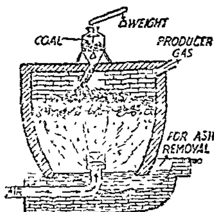


Fig. 48·2—Manufacture of producer gas.

Producer gas contains about 30—40 per cent nitrogen, 2—5 per cent hydrogen with some carbon dioxide.

It is an important by-product obtained during a number of metallurgical and other industrial operations. For example, it is present in the blast furnace gas.

Its principal use in industry is as a gaseous fuel in various metallurgical and other operations. *During the Second World War* when the major part of petrol supplies was reserved for military use, *producer gas served the civilian population.* Various civilian motor vehicles were provided with gas plants and run with producer gas. Charcoal was used for the manufacture of producer gas.

6. **Semi-water Gas.**—During the manufacture of water gas, we have seen that water gas is obtained during the "steam run" while during the "air run" we get producer gas. If the latter is not allowed to escape into the atmosphere but mixed with water gas, the mixture is called semi-water gas and used as a fuel.

7. **Coal Gas.**—The volatile products obtained by destructive distillation of coal are passed through water to free them from soluble and tarry matter. The residual gas is called *coal gas* and is an important gaseous fuel. About 95 per cent of coal gas consists

of combustible gases (H_2, CH_4, C_2H_4 and C_2H_2) with about 5% of non-combustible impurities (N_2=4%, CO_2=1%).

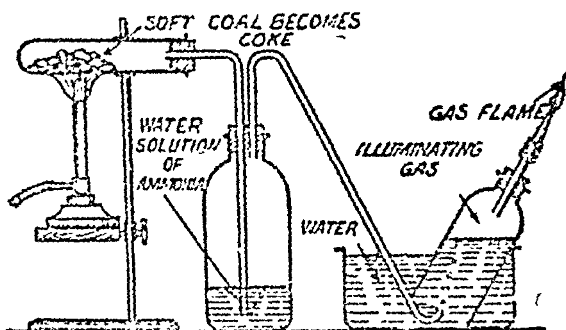


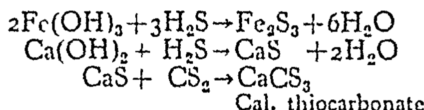
Fig. 48·3—Laboratory demonstration of the manufacture of coal gas.

Expt. 1. Heat some coal in a hard glass test tube and bubble the volatile product evolved through water contained in a wash bottle (Fig. 48·3). The soluble constituents dissolve here whereas the insoluble constituents pass up and are collected over water in a bottle fitted with a jet tube. On applying the flame to the jet, we find that the issuing gas burns with a luminous flame.

Manufacture of Coal Gas. The plant used is shown in the diagram (Fig. 48·4). Coal is placed in fire-clay retorts and heated externally in a gas-fired furnace to 900—1440°C. At the lower temperature the yield of the gas is poor but the quality of gas is better; while at higher temperature poor quality gas is obtained though large in quantity.

The gas evolved is passed through the **hydraulic main** and then through **condensers**. Here it loses its soluble constituents and tarry matter which overflows through the overflow pipe into the tar well.

It is further washed by passing up the scrubber, a tower packed with coke down which cold water is flowing. Any volatile sulphur compounds, *e.g.*, carbon disulphide, hydrogen sulphide, are removed by absorption in hydrated ferric oxide and slaked lime in purifiers.



$$2Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O$$
$$Ca(OH)_2 + H_2S \rightarrow CaS + 2H_2O$$
$$CaS + CS_2 \rightarrow \underset{\text{Cal. thiocarbonate}}{CaCS_3}$$

The gas thus purified is collected in the gas holders. A pump provided between the condensers and the scrubber maintains a steady flow of the gas through the plant.

Its Chief Uses. (*i*) As a gaseous fuel.

(*ii*) As an illuminant. Illuminating power of coal gas flame is due to the presence of unsaturated hydrocarbons, *e.g.*, ethylene and aromatic hydrocarbons, *e.g.*, benzene and naphthalene vapours.

(*iii*) For providing an inert or reducing atmosphere in various metallurgical or other operations.

Important By-products. Destructive distillation of coal for the manufacture of gas yields a number of important by-products given below :

(i) Coal-tar. It is a thick black liquid which collects in the tar well and is used for the manufacture of a large number of

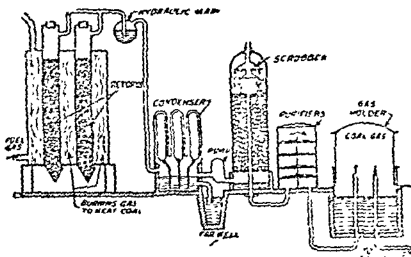


Fig. 48·4—Manufacture of coal gas.

organic compounds, e.g., benzene, toluene, naphthalene, phenol, anthracene, etc. These are used for the manufacture of dyes, drugs, explosives, disinfectants and perfumes.

(ii) Ammoniacal Liquor. This is the aqueous layer which floats over coal-tar and is used for the manufacture of ammonia.

(iii) Coke It is the non-volatile residue left in the retorts. It is used as fuel and as a reducing agent.

(iv) Gas Carbon. This is carbon scraped from the walls of retorts and is used for the manufacture of carbon electrodes.

Composition of Coal Gas. Coal gas is a mixture of several gases These gases fall into several groups, viz., illuminants, diluents and impurities. These

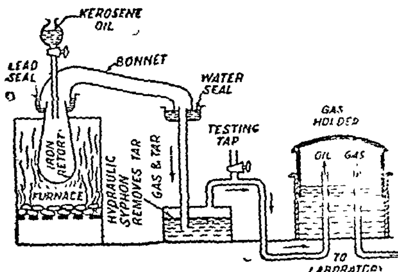


Fig. 48·5—Oil gas plant used in the laboratory.

illuminants are hydrocarbons and impart light to the flame. The diluents make the flame less smoky. The approximate composition by volume is as follow :

Hydrogen	45—55%	Nitrogen	2—12%
Methane	25—35%	CO_2	0—3%
CO, etc.	4—11%	Oxygen	0—1·5%
Ethylene, acetylene, benzene, etc. 2·5—6%			

8. **Oil Gas.**—Oil gas used in our laboratory is obtained by *cracking* kerosene in an oil gas plant (Fig. 48·5). The oil is dropped slowly in a thin stream over the red hot surface of an iron retort heated externally in a furnace. As soon as a drop of oil falls on the red hot surface, it breaks up at once into simpler hydrocarbons, saturated and unsaturated, *e.g.*, ethylene, acetylene, methane, etc. *The process of breaking up of higher hydrocarbons (in kerosene) into simpler hydrocarbons is called* cracking *and is an irreversible process.*

The gases produced rise up through the bonnet and then pass through a hydraulic syphon where they are freed from tarry matter and stored in a gas holder. Here it is mixed with an excess of air and supplied to the laboratory. The quantity of the gas is tested by taking a sample through the testing tap.

9. Natural Gas.—Putrefaction of vegetable matter under water yields marsh gas or methane, CH_4. This is the principal constituent of natural gas which issues from wells mainly situated in the oil producing regions. It is an excellent fuel which can be secured at relatively low cost. From the producing centres it is conducted to distant places through long pipe-lines. Thus it is one of the most valuable natural resources of the world.

QUESTIONS

Essay-type Questions

1. What are gaseous fuels and what is their importance in industry ? Mention the common types of gaseous fuels and their components. Describe, giving equations, the preparation of the gaseous fuels obtainable from coke. *(Dehi Pre-Medical 1961)*

2. Describe the preparation of producer gas and explain its uses in industry. In what way producer gas served the civilian population during the Second World War ? *(Bihar H.S. 1966)*

3. Describe the manufacture of oil gas used in your laboratory ?

4. Describe briefly the manufacture of coal gas giving line diagram. What are the useful by-products of this process and what is their importance in industry ? *(M.P. Board 1964)*

5. Describe in detail the manufacture of water gas. *(Bihar H.S. 1966, 62 Supp.)*

Test Your Understanding

6. Fill in the blanks in the following :

(i) Any combustible substance which may be burnt to supply heat energy without production of excessively objectionable .. is called a .

(ii) Requisites of a good fuel are : (1) It should be .., (2) should yield... , (3) should have a high......, and (4) should not give on burning any undesirable.. ...

(iii) Water gas is a mixture of......and..... obtained by passing .....over white hot......

(iv) Producer gas is essentially a mixture of .....and .....obtained by burning.. . in a limited supply of......

(v) The process of breaking up of higher hydrocarbons into simpler ones is called......

(vi) ......is the principal constituent of natural gas.

KEY

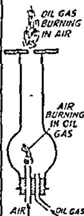
(i) by-products, fuel ; (ii) cheap, little ash, heat content, products ; (iii) CO, H_2, steam, coke ; (iv) CO, N_2, coke, air ; (v) cracking ; (vi) Methane.

COMBUSTION AND FLAME

COMBUSTION IS ANY CHEMICAL ACTION WHICH OCCURS PRODUCING NOTICEABLE HEAT AND LIGHT (e g , BURNING OF Mg RIBBON)

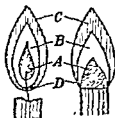
SPONT NEOUS COMBUSTION IS THE COMBUSTION DEVELOPING AS A RESULT OF MERE SLOW OXIDATION (e g., BURNING OF HEAP OF OILY RAGS).

49



TERMS COMBUSTIBLE AND SUPPORTER OF COMBUSTION ARE RELATIVE

A FLAME IS A ZONE OF BURNING GAS



A-ZONE OF NO COMBUSTION
B- " " PARTIAL "
C- " " COMPLETE " "
D- BLUE ZONE.

Combustion and Flame

1. Combustion.—Hold a piece of magnesium ribbon in a Bunsen flame, it catches fire and burns with a dazzling white light. *Any chemical action, like burning of magnesium, which occurs producing noticeable heat and light is termed Combustion.* A few other examples of combustion are—burning of candle, a jet of hydrogen burning in chlorine. Glowing of an electric lamp is accompanied by production of both heat and light but it is not combustion as no chemical reaction is involved and combustion is necessarily a chemical action accompanied by production of heat and light.

2. Spontaneous Combustion.—Sometimes heaps of coal dust, hay or oily rags catch fire even when no flame or spark is brought near them. Lying in air, they undergo a process of slow oxidation accompanied by evolution of heat. The materials being poor conductors of heat, the heat accumlates in them thus constantly increasing the rate of reaction and raising the temperature. These may finally become hot enough to burst into flame.

The combustion developing as a result of mere slow oxidation is known as spontaneous combustion.

3. Combustible and Supporter of Combustion.—Substances burn in oxygen but oxygen itself does not burn. For example, a jet of hydrogen burns in oxygen Here hydrogen which burns is called *combustible* and oxygen which allows hydrogen to burn in it, i.e., supports the combustion of hydrogen, is called a *supporter of combustion.*

In general the substance that burns is termed **combustible** while the medium in which combustion takes place is called **supporter of combustion.** The following experiment as well as the one given on page 2·7 will illustrate that the terms combustible and supporter of combustion are relative terms.

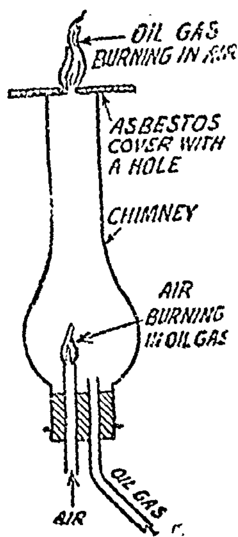


Fig. 49·1→Experiment to show that the terms 'combustible' and 'supporter of combustion' are relative.

Expt. 1. Fit the lower end of a chimney with a cork through which two tubes are passing and cover the upper end with cardboard having a hole at the centre. Close the hole, connect one of the tubes with a gas tap and light the gas at the lower end of the second tube.

Open the hole at the top and light the gas at the hole. The suction produced by the flame will drag the flame from the lower end to the upper end of the tube.

Now we have two flames (Fig. 49·1) (*i*) air burning in oil gas inside the chimney, and (*ii*) oil gas burning in the air at the top. Thus air is combustible in the first case and supporter of combustion in the other while oil gas is supporter of combustion in the first case and combustible in the second. This shows that two terms are interchangeable.

4. **Flame.**—*A flame is a zone of burning gas.* Most of the gases burn readily when mixed with oxygen or air. Volatile liquids, *e.g.*, gasoline and kerosene, first vaporise and then their vapours burn. Solids like wood and wax which produce gaseous products are found to burn with a visible flame. Charcoal, coke and hard coal glow as they burn. They produce little or no flame as they contain little volatile matter.

5. **Ignition Temperature.**—Every combustible material must be heated to a certain temperature before it begins to burn. *The lowest temperature at which a substance catches fire or begins to burn is called its* **ignition temperature or kindling temperature.** Every substance has its own characteristic ignition temperature. For example, white phosphorus has a very low ignition temperature with the result that warmth of the hand is enough to kindle it. Ignition temperature of sulphur is pretty high. A burning substance is at once extinguished as its temperature falls below the ignition temperature.

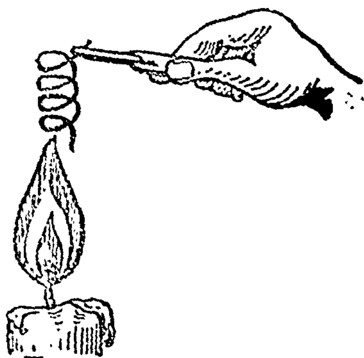


Fig. 49·2—A burning candle is extinguished as its temperature falls below the ignition temperature.

Expt. 2. Lower a copper spiral into the flame of burning candle. The candle is extinguished. Copper spiral absorbs heat from the flame and cools it below the ignition temperature, and the candle is extinguished.

In extinguishing fire we try to accomplish one or more of the following :

(i) Cut off the supply of air, the supporter of combustion. For example, we surround the burning substance by carbon dioxide. foam or even sand.

(ii) Cool the burning object below its ignition temperature. Pouring water over fire lowers its temperature and water vapours produced shut off the supply of oxygen.

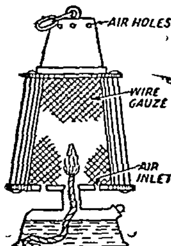


Fig 49 3 · avy s safety lamp.

(iii) Remove the combustible material. For example, when a laboratory table catches fire, the first step in putting out the fire is to cut off the supply of oil gas from the room.

6. **Davy's Safety Lamp.**—Naked flames had caused many disastrous explosions in mines. Davy in his safety lamp surrounded the flame by a wire-gauze screen. This being a good conductor of heat absorbed heat of the flame and radiated it uniformly in all directions. The temperature of the surrounding combustible gases, if any, was thus not allowed to reach the ignition point.

7. **Structure of the Flame.**—Flames are hollow and are made up of several distinct zones or cones. Flame given by burning hydrogen is the simplest, being made up of only two cones. In the inner cone there is no combustion whereas in the outer cone there is combustion. Such flames, as that of hydrogen, are called **single mantled flames.**


Fig. 49·4—Hydrogen flame.

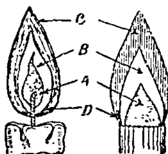


Fig. 49·5—The parts of a Bunsen or a candle flame.

The flame of Bunsen burner or a candle is made up of four cones and is called a **double mantled flame.** The different parts of a Bunsen or a candle flame as shown in Fig. 49·5 are :

(i) **Zone of no-combustion, 'A'** contains unburnt gas particles. A tip of the match stick placed in this zone does not catch fire showing that it is a zone of no-combustion.

If one end of a glass tube is placed in this zone, the unburnt gas particles present in it can be lighted at the other end of the glass tube.

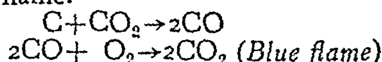
(*ii*) **Zone of partial combustion,** '*B*' surrounds '*A*'. Here the various hydrocarbons present in the oil gas decompose into free carbon and hydrogen. This is the luminous part of the flame

(*iii*) **Zone of complete combustion,** '*C*' is the non-luminous mantle surrounding '*B*'. It can be made visible by bringing a copper chloride crystal near the flame when a blue mantle is seen surrounding '*B*'. This is the hottest part of the flame. Here carbon and hydrogen produced in '*B*' are completely oxidised to carbon dioxide and water vapour.



Robert W. Bunsen (1811–99) German chemist who invented the burner known after his name.

(*iv*) **Blue Zone,** '*D*'. At the base *carbon monoxide produced* by interaction of carbon particles from lower part of '*A*' with carbon dioxide from the lower part of '*C*', burns with a blue flame.



$$C + CO_2 \rightarrow 2CO$$
$$2CO + O_2 \rightarrow 2CO_2 \text{ (Blue flame)}$$

8. Striking back of Bunsen Flame.—When oil gas containing hydrocarbon is to be used for heating purposes, its complete combustion without any intermediate liberation of free carbon, is desirable. In a Bunsen burner, this is achieved by admitting air through the air holes near the bottom of the burner tube. This air mixes with the gas before the latter reaches the flame. It cools the inner zone of the flame and prevents the dissociation of gas to give free carbon. The flame produced is non-luminous.

If, however, too much of air is admitted, the flame travels down into the barrel of the burner, the gas begins to burn at the end of the nipple down below. This is called striking back of the burner. To prevent 'striking back' air holes should be only partially opened to admit just the desired quantity of air.

9. The Luminosity of Flames.—Presence of solid particles was considered by Davy to be the only cause of the luminosity of flames. Hydrogen and carbon monoxide burn with a non-luminous flame as there are no solid particles present in these gases. Magnesium burns with a luminous flame due to the presence of solid magnesium oxide particles which become incandescent in the flame. Further proof of this view is afforded by the fact that non-luminous flames can be made luminous by introduction of the solid particles in them.

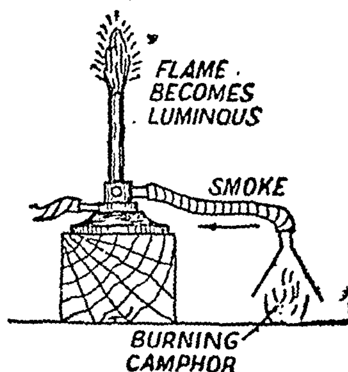


Fig. 49·6—Non-luminous flame is made luminous by camphor particles.

[illegible] a non- [illegible] vapours [illegible] and a [illegible]

Expt. 4. Take a Y-tube and put an asbestos plug dipped in benzene in one of its limbs (Fig. 49·7). Connect the lower end of the Y-tube with the gas tap and light the gas issuing from the other two ends. Gas issuing through the benzene plug burns with a luminous flame whereas the gas escaping through the other end burns with a non-luminous flame.

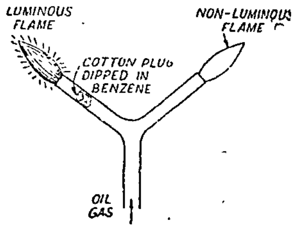


Fig. 49·7—Causes of luminosity of flame.

Some other factors on which the luminosity of a flame depends are :

(i) **Density of the gases.** Hydrogen which burns with a non-luminous flame under ordinary pressure, burns with a luminous flame when compressed to about 10—12 atmospheres pressure.

(ii) **Temperature.** A non-luminous flame can be made luminous by heating the burner tube. When a burner strikes back, the flame becomes luminous and the tube of the burner is found to be too hot to touch.

10. **Gas Mantles.** Water gas burns with a non-luminous [illegible] Welsbach gas mantles.

Gas mantles consist of artificial silk pouches. These are impregnated with a mixture of thorium and cerium nitrates. On ignition the nitrates yield a mixture of thorium and cerium oxides. When the mantle is held in the non-luminous gas flame, these oxide particles become incandescent and emit light.

11. **Temperature of Commoner Flames.**—Appliances used for measuring high temperatures are called pyrometers. It would be interesting to note the average temperatures of the commer flames we come across.

Sun (outer part)	7000°C	Oxy-hydrogen blowpipe	[illegible]
Oxy-acetylene blowpipe	3000°—4000°C	Blowpipe burner	[illegible]
Electric arc	3500°C	Bunsen burner	[illegible]

QUESTIONS

Essay-type Questions

1. What do you understand by combustion ? [illegible] rusting ? [illegible]

2. What do you understand by combustion, supporter of [illegible] and a combustible substance ? In a Bunsen flame there is a [illegible] and an oxidising area. In the diagram of the flame indicate these areas and explain their importance in the dry tests of analysis.

3. Draw the neat diagram of a Bunsen flame and label the different parts. What chemical reactions take place in the different parts? What are the causes of the luminosity of the flame? *(Delhi H.S. 1967, 60)*

4. Distinguish between combustion and oxidation. Describe an experiment to show that the terms Combustible and Supporter of Combustion in case of gases are interchangeable. How do you account for the brilliancy of the light given out when mantles are used with a non-luminous gas flame for producing light? *(Punjab H.S. 1962)*

5. What is a flame and what are the essential conditions for its formation? Discuss the nature of combustion and the causes of luminosity of a flame.

Describe Davy's safety lamp and its working mentioning the principles on which its use is based. *(All India H.S. 1967)*

6. Write a short note on the causes of Luminosity of a Flame. *(Delhi H.S. 1965, 60)*

7. Write short notes on :

(i) Combustion. *(Delhi H.S. 1963)*

(ii) Combustion and flame.

8. Explain the structure of flames produced by (*a*) hydrogen burning in air, (*b*) coal gas when burnt with a visible air supply as in a Bunsen burner. Describe experiments in support of your statement.

9. Write a short note on Structure and Luminosity of Bunsen flame and its striking back. *(All India H.S. 1969, 67 ; Delhi H.S. 1965, 63)*

10. How do you account for the brilliancy of the light given out when mantles are used with a non-luminous gas flame for producing light.

Test Your Understanding

11. Fill in the blanks in the following :

(i) Any chemical action like burning of magnesium which occurs producing noticeable heat and light is termed......

(ii) A combustion developing as a result of mere......is known as spontaneous combustion.

(iii) A......is a zone of burning gas.

(iv) The lowest temperature at which a substance catches fire is termed......or......

(v) For extinguishing fire try to cut off the......, cool the burning object below its......and remove the......

(vi) Luminosity of flame depends on......, ...and......

KEY

(i) combustion ; (ii) slow oxidation ; (iii) flame ; (iv) ignition temperature, kindling temperature ; (v) supply of air, ignition temperature, combustible material ; (vi) presence of solid particles, density of gases, temperature.

BORON (IN GROUP III A) AND SILICON (IN GROUP IV A) EXHIBIT DIAGONAL RELATIONSHIP

IA																	0
H	IIA											IIIA	IVA	VA	VIA	VIIA	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	Al	Si	P	S	Cl	Ar
												Ga	Ge				
													Sn				
													Pb				

50

(i) BOTH ARE NON-METALS WITH HIGH M.P. AND ARE BAD CONDUCTORS OF ELECTRICITY

(ii) BOTH GIVE ACIDIC OXIDES BORATES RESEMBLE SILICATES.

(iii) BOTH GIVE SIMILAR HALIDES AND HYDRIDES.

(iv) BOTH EXIST IN ALLOTROPIC FORMS.

Boron and Silicon

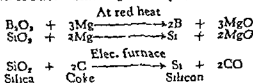
1. General.—Boron is grouped with aluminium and other elements and placed in Group III A of the periodic table. Silicon is grouped with carbon and placed in Group IV A.

Boron resembles aluminium, it being trivalent. Both burn and form oxides when strongly heated and liberate hydrogen when reacted with caustic alkalis.

Silicon resembles carbon in being a tetravalent element with a high melting point. Both show allotropy and form similar acidic dioxides Main difference between them is the capacity of carbon atoms to form long chains.

Boron and silicon show a close resemblance in their properties. For example,

(i) Both are prepared by similar methods. For instance, boron is prepared by reduction of boron trioxide with magnesium powder and silicon is obtained by reduction of silicon with magnesium powder or coke.



$$B_2O_3 + 3Mg \xrightarrow{\text{At red heat}} 2B + 3MgO$$
$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$
$$\underset{\text{Silica}}{SiO_2} + \underset{\text{Coke}}{2C} \xrightarrow{\text{Elec. furnace}} \underset{\text{Silicon}}{Si} + 2CO$$

(ii) Both are non-metals with high melting points and are bad conductors of electricity.

(iii) Both give acidic oxides. Borates resemble silicates and are obtained when acidic oxides are dissolved in alkalis.

(iv) Both give similar halides (e g., BF_3 and SiF_4) which are easily hydrolysed and both give similar hydrides.

(v) Both exist in allotropic forms.

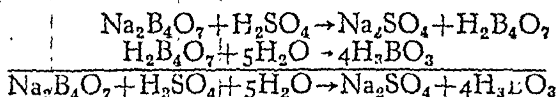
COMPOUNDS OF BORON AND SILICON

2. Ortho Boric Acid, H_3BO_3.

Preparation. (i) From Tuscan Soffioni. Jets of steam called *Soffioni* that issue from the ground in certain pa-- -f

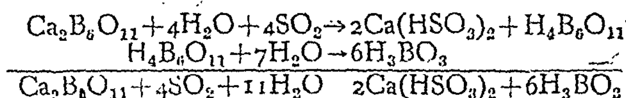
Tuscany contain boric acid. These are passed through water lagoons. Solution of boric acid is periodically removed from these lagoons, concentrated and crystallised.

(*ii*) **From Borax.** On a small scale boric acid is prepared by treating a concentrated solution of borax with a calculated quantity of concentrated sulphuric acid. On cooling, crystals of boric acid separate.



$$Na_2B_4O_7 + H_2SO_4 \rightarrow Na_2SO_4 + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O \rightarrow 4H_3BO_3$$
$$\overline{Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3}$$

(*iii*) **From Colemanite.** By passing sulphur dioxide through colemanite suspended in water.



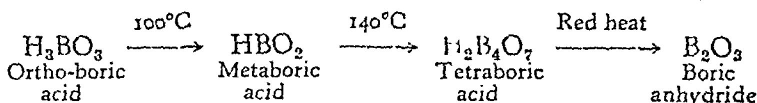
$$Ca_2B_6O_{11} + 4H_2O + 4SO_2 \rightarrow 2Ca(HSO_3)_2 + H_4B_6O_{11}$$
$$H_4B_6O_{11} + 7H_2O \rightarrow 6H_3BO_3$$
$$\overline{Ca_2B_6O_{11} + 4SO_2 + 11H_2O \quad 2Ca(HSO_3)_2 + 6H_3BO_3}$$

The crystals of boric acid separate out on cooling.

Properties. It is a white crystalline substance soft and soapy to touch. It is slightly soluble in cold water, more so in hot and is volatile in steam.

(*i*) It is a weak acid and in solution gives only a wine red colour with litmus.

(*ii*) On heating it decomposes as indicated below :



$$\underset{\text{Ortho-boric acid}}{H_3BO_3} \xrightarrow{100°C} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{140°C} \underset{\text{Tetraboric acid}}{H_2B_4O_7} \xrightarrow{\text{Red heat}} \underset{\text{Boric anhydride}}{B_2O_3}$$

(*iii*) It turns turmeric paper brown which turns blackish on dipping in sodium hydroxide.

(*iv*) A mixture of ethyl alcohol with boric acid burns with a green-edged flame due to the formation of ethyl borate.

Uses. (*i*) As an antiseptic and in medicine.

(*ii*) As a preservative of food.

(*iii*) In making enamels and pottery glazes.

(*iv*) In glass industry.

Test for Boric acid and Borates.

(i) *Action of Heat.* Borates generally swell upon heating.

(ii) *Flame test.* These impart a green colour to flame.

(iii) *Green-edged flame Test.* A paste of concentrated sulphuric acid and alcohol with boric acid or borates burns with green-edged flame.

(iv) *Turmeric paper Test.* A borate solution is acidified with dilute hydrochloric acid. A turmeric paper is dipped in this solution and dried when it gives a brown colour which changes to greenish black on dipping in caustic soda solution.

3. **Borax, Sodium tetraborate, $Na_2B_4O_7$ (सुहागा).**

Tincal, a crude form of borax, contains about 55 per cent of it and is found in inland dried-up lakes of Tibet, Ceylon and California.

Preparation. Methods employed for the preparation of borax are :

(i) **From Colemanite.** The mineral borate is boiled with a concentrated solution of sodium carbonate.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}} + 2Na_2CO_3 \rightarrow 2CaCO_3 + \underset{\text{Borax}}{Na_2B_4O_7} + \underset{\text{Sodium metaborate}}{2NaBO_2}$$

On filtration and concentration of filtrate, crystals of borax separate. A current of carbon dioxide is passed through the mother liquor to convert the metaborate into borax.

$$4NaBO_2 + CO_2 \rightarrow Na_2CO_3 + Na_2B_4O_7$$

(ii) **From Tincal.** Naturally-occurring crude borax (Tincal) is dissolved in water, filtered, concentrated and crystallized when pure borax is obtained.

Properties. It is a colourless, crystalline substance. The hydrated crystals of borax lose their water of crystallization on heating and swell.

(i) *Hydrolysis.* Its solution is slightly alkaline due to hydrolysis.

$$Na_2B_4O_7 + 2H_2O \rightleftharpoons 2NaOH + H_2B_4O_7$$

(ii) *Borax bead.* With certain metallic salts it gives coloured beads due to the formation of metal metaborates.

$$\underset{\text{Borax}}{Na_2B_4O_7} + \underset{\text{Cobalt oxide}}{CoO} \rightarrow \underset{\text{Sod. metaborate}}{2NaBO_2} + \underset{\text{Cobalt metaborate (Blue)}}{Co(BO_2)_2}$$

Uses. (i) In borax bead test.

(ii) In enamelling and pottery glaze.

(iii) As a flux in soldering and welding.

(iv) For impregnating match sticks to prevent after-glow.

(v) As a preservative.

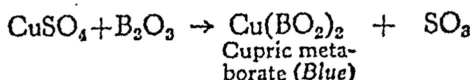
4. **Borax Bead Test.**—This is a *dry test* applied for the identification of coloured salts and is performed as under :

A little borax is taken in a platinum loop, and heated in flame when it swells and then fuses to give a colourless glassy bead. This is dipped in the solution of the coloured salt and heated strongly when a characteristic colour is imparted to the bead and gives an indication of the nature of the basic radical present.

This colour is due to the formation of metaborates with characteristic colours. For example, in the case of copper salts the blue or colourless bead is obtained as follows :

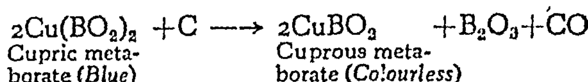
$$\underset{\text{Borax}}{Na_2B_4O_7.10H_2O} \rightarrow Na_2B_4O_7 \rightarrow \underset{\text{Sod. metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

(*i*) *In oxidising flame.*

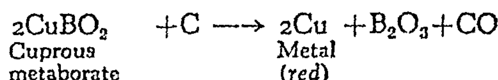


$$CuSO_4 + B_2O_3 \rightarrow \underset{\text{Cupric meta-borate (Blue)}}{Cu(BO_2)_2} + SO_3$$

(*ii*) *In reducing flame.*



$$\underset{\text{Cupric meta-borate (Blue)}}{2Cu(BO_2)_2} + C \longrightarrow \underset{\text{Cuprous meta-borate (Colourless)}}{2CuBO_2} + B_2O_3 + CO$$



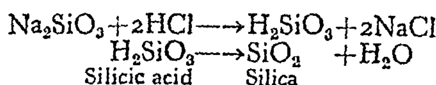
$$\underset{\text{Cuprous metaborate}}{2CuBO_2} + C \longrightarrow \underset{\text{Metal (red)}}{2Cu} + B_2O_3 + CO$$

Similarly characteristic colours are obtained with chromium, cobalt, manganese, nickel and iron salts.

Metal		Chromium	Cobalt	Man-ganese	Nickel	Iron
Colour in oxidizing flame	Hot	Green	Blue	Pinkish violet	—	Brown
	Cold	,,	,,	,,	Brown	Yellow
Colour in reducing flame	Hot	,,	,,	Colourless	—	Bottle green
	Cold	,,	,,	,,	Grey	,,

5. **Silica or Silicon dioxide, SiO_2.**—Different forms of silica occurring in nature are quartz, sand, flint, kieselguhr and certain precious stones, *e.g.*, opal, amethyst and agate. It is also found in plants and animals.

Chemically pure silica may be prepared in the laboratory by the action of acids on silicates and igniting the silicic acid obtained.



$$Na_2SiO_3 + 2HCl \longrightarrow H_2SiO_3 + 2NaCl$$

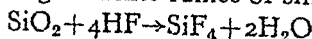
$$\underset{\text{Silicic acid}}{H_2SiO_3} \longrightarrow \underset{\text{Silica}}{SiO_2} + H_2O$$

Properties. (*a*) **Physical.** (*i*) Quartz, flint and agate are very hard and can be scratched or cut with diamond alone.

(*ii*) Different varieties are soluble in water and fuse at about 1700° to a transparent liquid.

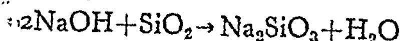
(*iii*) Its coefficient of expansion being low, a red hot silica crucible does not crack even when plunged into cold water.

(*b*) **Chemical.** (*i*) *Action of Acids.* Silica reacts with hydrofluoric acid alone to give white fumes of silicon tetrafluoride.



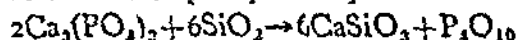
$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

(*ii*) *Acidic Nature.* It is acidic in nature and gives silicates when fused with alkalis.



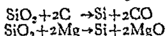
$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

With calcium phosphates on fusion in an electric furnace, it gives calcium silicate and phosphorus pentoxide.



$$2Ca_3(PO_4)_2+6SiO_2 \rightarrow 6CaSiO_3+P_4O_{10}$$

(iii) *Reduction.* It is reduced to silicon when heated with coke in an electric furnace or with magnesium powder.



$$SiO_2+2C \rightarrow Si+2CO$$
$$SiO_2+2Mg \rightarrow Si+2MgO$$

Uses. Different varieties of silica find varied uses as given below :

(i) Sand is used in the manufacture of glass and porcelain. It is used in the preparation of cement and mortar.

(ii) Silica vessels are used for strong acids and silica bricks are used for making acid resisting towers and as refractory material in lining furnaces.

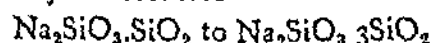
(iii) Quartz is used in the manufacture of lenses and prisms for spectacles and optical instruments. Coloured varieties are used as gems.

(iv) Fused quartz is used for making suspension fibres.

(v) Kieselguhr is used in the manufacture of dynamite, an explosive.

(vi) Sandstone is employed as a building material and for making millstones.

6. **Sodium silicate or Water glass.**—Chemically water glass is sodium silicate containing excess of silica. Its composition varies as represented by the formula



$$Na_2SiO_3.SiO_2 \text{ to } Na_2SiO_3\,3SiO_2$$

It is obtained by fusing sand and washing soda mixture in a furnace. The fused mass on solidification gives a glassy solid (soluble glass). This is powdered and dissolved in water under pressure to get the syrupy mass of 50—52 Be.

Water glass is soluble in water and on placing crystals of different salts in water glass solution (Sp. Gr. 1·1), beautiful growths are obtained which are called *Silica gardens* (Fig. 50·1).

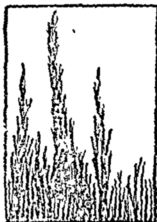


Fig 50·1—Silica garden.

Uses. Water glass is used :

(i) As a filler in the soap manufacture. In India it is used mainly for this purpose.

(ii) In calico printing.

(iii) For rendering textile and timber fire-proof.

(iv) As furniture polish and for preservation of eggs.

7. **Glass.**—Glass is transparent, hard and brittle when cold but softens on heating. Ordinary glass is a mixture of silicates of sodium and calcium and probably a solid solution of these in each other. As it is not a definite chemical compound, no definite formula can be assigned to it.

Raw materials required for glass industry. Various raw materials used are :

(*i*) *Silica* in the form of sand or quartz.

(*ii*) *Alkali metals* in the form of sodium sulphate or potassium carbonate.

(*iii*) *Alkaline earths* in the form of limestone ($CaCO_3$) or lime (CaO).

(*iv*) *Heavy metals* as litharge or red lead.

(*v*) *Oxdising agents* or decolorisers like manganese dioxide, potassium nitrate or sodium nitrate.

(*vi*) *Colouring materials* in the form of metallic oxide to get the desired colour, *e.g.*, CaO to get blue colour and Cr_2O_3 to get green colour.

Manufacture of Glass. The process is completed in three different stages as given below :

(*a*) **Fusion of Raw Materials.** The main raw materials are sand, limestone and washing soda. These are mixed in proper proportions and ground. The mixture is called *the batch.* This is mixed with a certain proportion of old broken glass known as cullet and heated to a high temperature in a gas fired tank furnace working on the regenerative principle of heat economy (Fig. 50·2). The addition of cullet melts the batch readily and uses up what would otherwise be a waste material. The whole mass fuses and a mixture of silicates is obtained. The heating is continued till the fused mass is free of carbon dioxide bubbles.

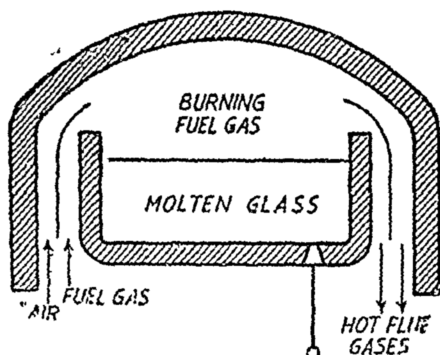
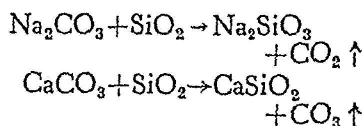


Fig. 50·2—A tank furnace for melting the batch.



$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \uparrow$$

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \uparrow$$

Coloured glass is obtained by addition of certain metallic radicals to the batch. Chromium produces a deep green colour, cobalt gives a pretty blue colour and manganese colours it amethyst or red. Traces of iron compounds present in sand as an impurity impart a pale green colour to glass.

(b) **Working of molten glass.** An expert glass blower rolls his blowpipe into the molten mass until the required amount of glass has adhered to its end. He then blows a bubble in the adhering mass and gives it the required shape with or without the help of a mould. In bigger factories the greater fraction of products is machine made while laboratory glassware and a few better grades of table glass are still manufactured by the hand-blown process.

(c) **Annealing.** The finished articles have to be cooled very slowly otherwise the glass is very brittle. These are made to travel on a slow moving belt through a long narrow chamber called a lehr. It is hot at one end and at room temperature at the other end. So slowly does the belt move that an article takes several days to pass through the lehr. This process of slow cooling of glass is called annealing.

Different Kinds of Glass. Some commoner varieties of glass obtained by varying the composition of the batch are :

(i) **Soft glass.** This is the ordinary soda-lime glass and is used for window glass and bottles.

(ii) **Hard glass** is ths potash-lime glass (Batch : sand+limestone+K_2CO_3) used for hard glass apparatus.

(iii) **Optical glass** is lead-potash glass (Batch : sand+red lead+K_2CO_3) and is a more lustrous product.

(iv) **Jena and Pyrex glass** is sodium aluminium borosilicate glass and can withstand wide changes in temperature.

(v) **Reinforced glass** has a network of wires embedded in it and shatter proof glass is obtained by cementing two glass plates with some plastic.

(vi) **Quartz glass or Silica glass** is obtained from pure silica. It has a low coefficient of expansion and does not break even when plunged in water while red hot.

(vii) **Glass wool.** Glass fibres are obtained by forcing molten glass through tiny holes in the presence of a jet of high pressure steam. These are spun into yarn and woven into cloth used for making fire-proof dresses and heat insulating curtains.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between .

1. Red hot magnesium+(i) Silica (ii) Boron trioxide.
2. Silica+Coke (in electric furnace)
3. Borax+(i) Conc. sulphuric acid (ii) Water (hydrolysis).
4. Colemanite+(i) Sulphur dioxide, (ii) Sodium carbonate.
5. Action of heat on (i) Orthoboric acid, (ii) Silicic acid.
6. Sodium meta borate+Carbon dioxide.
7. Borax+Cobalt salt in a borax bead.
8. Sodium silicate and Hydrochloric acid.
9. Silica+(i) Hydrofluoric acid, (ii) Caustic soda, (iii) Calcium phosphate, (iv) Sodium carbonate, (v) Calcium carbonate.

QUESTIONS

Essay-type Questions

1. How many of the following terms can you define or explain ?

Colemanite	Tincal	Orthoboric acid
Silica gardens	Borax	Metaboric acid
Glass wool	Silica	Tetraboric acid
Cullet	Annealing	Borax bed test
Batch	Lehr	Reinforced glass.

2. Compare the physical and chemical properties of boron and silicon.

3. How is boric acid prepared ? Mention some of its important properties and uses. *(Delhi H.S. 1968, 67, 66, 65, 61)*

4. Give the preparation, properties and uses of Borax. *(Delhi Pre-Medical 1963 ; All India H.S. 1968, 67 ; Punjab Pre-Univ. 1971)*

5. What are the different naturally-occurring compounds of boron ? How can boron be obtained from those compounds ?

[Hint. Different naturally-occurring compounds of boron are boric acid, borax and colemanite. These may be converted into boric acid (*see* page 2·259) which gives boron trioxide at red heat. Boron is prepared by reduction of boron trioxide with magnesium powder.]

6. Write a short note on 'Chemistry of the borax bead test'. *(Delhi H.S. 1964, 63)*

7. Give the preparation, properties and uses of water glass (sodium silicate). *(Delhi H.S. 1972, 70, 69, 66)*

8. Write an account of the manufacture of glass. What is hard and soft glass ? How are coloured or opalescent glasses obtained ? What is water glass and how does it differ in its chemical composition, properties and uses from ordinary glass ? *(All India H.S. 1966 ; Delhi H.S. 1964, 63 ; Delhi Pre-Univ. 1969 ; M.P. Board 1964)*

9. What is the composition of glass ? How is it manufactured ? Give its properties and uses. *(All India H.S. 1966)*

10. Give the preparation, properties and uses of sodium silicate. *(Delhi H.S. 1969, 67)*

11. (*a*) Write an essay on Glass Industry.
(*b*) Write a short note on "Annealing".
(*c*) Give the preparation and uses of silica.

Test Your Understanding

12. Fill in the blanks in the following :

(*i*) Boron in Group......and silicon in group......show a......relationship ;

(*ii*) Both boron and silicon give......oxides which dissolve in......to form......and......respectively.

(*iii*) $Ca_2B_6O_{11}$ is......and $Na_2B_4O_7$ is ..... ;

(*iv*) $H_3BO_3 \xrightarrow{100^\circ C} ...... \xrightarrow{140^\circ C} ...... \xrightarrow{\text{Red heat}} ......$
....

(*v*) Ordinary glass is a mixture of......of......and......It is probably a ......solution of these and not a definite......hence no definite...... can be assigned to it.

(*vi*) Finished glass articles have to be cooled very slowly, otherwise the glass becomes...... ;

(*vii*) The hot glass articles are made to travel on a .....through a long narrow chamber called a......for slow cooling. This process of slow cooling of glass is termed .....

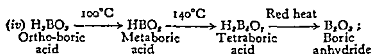
(*viii*) Soft glass is .....glass, hard glass is .....glass, optical glass is...... glass and pyrex glass is .... glass.

KEY

(*i*) IIIA, IVA, diagonal ;

(*ii*) acidic, alkalis, borates, silicates ;

(*iii*) Colemanite, borax ;



(*iv*) $H_3BO_3 \xrightarrow{100°C} HBO_2 \xrightarrow{140°C} H_2B_4O_7 \xrightarrow{\text{Red heat}} B_2O_3$;
Ortho-boric acid, Metaboric acid, Tetraboric acid, Boric anhydride

(*v*) silicates, sodium, calcium, solid, chemical compound, formula ;

(*vi*) very brittle ;

(*vii*) slow moving belt, lehr, annealing ;

(*viii*) soda-lime, potash lime, lead-potash, sodium aluminium borosilicate.

Appendix

NEW TYPE TEST PAPER II

(Based on Chapters 28 to 50)

Completion Test

1. Fill in the blanks with a correct word or words in the following statements :

(*i*) Oxygen may be obtained by the action of water on......

(*ii*) In the fractional evaporation of air......escapes first because it is more......

(*iii*) Hydrogen may be obtained from water by (*a*)......(*b*)...... (*c*)......

(*iv*) Hydrogen is manufactured by passing alternate currents of......and...... over......(Lane's Process).

(*v*) Pure hydrogen may be obtained by the action of...... on......

(*vi*) Water reacts with metallic oxides to form......and with oxides of non-metals to form......

(*vii*) Hardness of water is due to the presence of......

(*viii*) In the Clark's method, water is softened by......

(*ix*) Barium peroxide is decomposed by......or by......to form hydrogen peroxide.

(*x*) Permutit is obtained by fusing together......, ...and ......

2. Fill in the blanks with a correct word or words in the following statements :

(*i*) The percentage of oxygen is approximately......per cent in the atmosphere and......per cent in the earth's crust.

(*ii*) Combination of substances with oxygen with the evolution of heat and light is called......

(*iii*) The process of soaking up only on the surface is called ......or......

(*iv*) Hydrogen is used in the manufacture of......, ..., ... and......

(*v*) Oxidation is any process of involving addition of......or any other......radical or any process involving removal of......or any other......radical.

(*vi*) Reaction in which oxidation and reduction take place simultaneously are called......reactions.

True-False Test

3 In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements :

(i) *Potassium permanganate* gives oxygen on heating.

(ii) Oxygen is absorbed by *alkaline pyrogallol.*

(iii) When palladium is heated in an atmosphere of hydrogen, the gas is soaked up *through the entire mass of* the metal.

(iv) Liquid oils absorb hydrogen in the presence of finely divided *iron.*

(v) Presence of bicarbonates of calcium and magnesium causes *temporary hardness.*

(vi) The exhausted permutit can be regenerated by soaking it with a solution of *calcium chloride.*

(vii) Hydrogen peroxide is manufactured by the electrolysis of 50 *per cent sulphuric acid* followed by vacuum *distillation.*

(viii) Hydrogen peroxide possesses *acidic* nature.

4. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements:

(i) Oxygen is obtained as a by-product in the manufacture of hydrogen by *electrolysis* of water.

(ii) Hydrogen peroxide is a valuable *bleaching agent and a germicide.*

(iii) Hydrogen peroxide is a *reducing agent.*

(iv) The oxides of metals which unite with water to form *acids* are called *acid anhydrides.*

Selection Test

5. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(i) Oxygen is obtained on heating (*a*) manganese dioxide, (*b*) calcium oxide, (*c*) washing soda

(ii) When oxygen is mixed with nitric oxide (*a*) no visible change takes place, (*b*) reddish brown vapours are formed, (*c*) the mixture becomes very hot.

(iii) Ferric chloride is reduced by (*a*) ordinary hydrogen, (*b*) nascent hydrogen, (*c*) ordinary hydrogen in presence of a catalyst.

(iv) Hydrogen may be obtained by heating a solution of alkali with (*a*) zinc, (*b*) iron, (*c*) magnesium.

(v) SO_2, CO_2 and oxides of nitrogen may be removed from hydrogen by passing it through (*a*) strong caustic potash solution, (*b*) strong potassium permanganate solution, (*c*) through silver nitrate solution.

(vi) Calgon is the trade name of (*a*) an *artificial zeolite*, (*b*) an ion exchange resin, (*c*) sodium hexa-metaphosphate.

(*vii*) When hydrogen peroxide is shaken with potassium dichromate solution in sulphuric acid and ether, the ethereal layer (*a*) becomes orange colour, (*b*) turns blue, (*c*) remains colourless.

6. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) Oxygen is manufactured by the fractional evaporation of (*a*) water, (*b*) liquid air, (*c*) hydrogen peroxide.

(*ii*) With a solution of titanium oxide hydrogen peroxide gives (*a*) orange colour, (*b*) blue colour, (*c*) no colour.

(*iii*) Calgon is the trade name of (*a*) calcium phosphate, (*b*) sodium hexametaphosphate, (*c*) sodium aluminosilicate.

(*iv*) Hydrogenation of oils is carried on by passing hydrogen through the oil in the presence of finely divided (*a*) platinum, (*b*) nickel, (*c*) iron.

(*v*) Hydrogen peroxide is (*a*) an oxidising agent, (*b*) a reducing agent, (*c*) both an oxidising as well as reducing agent.

Matching Test

7. Mark each item in list II with appropriate numbers—(*i*), (*ii*), (*iii*), etc. so that it becomes related with the corresponding items in list I. One of these has been marked for you as an example.

List I	List II
(*i*) Oxidation	(...) Combination with oxygen with evolution of heat and light.
(*ii*) Oxylithi	(...) Addition of oxygen.
(*iii*) Combustion	(...) Calcium hydride.
(*iv*) Occlusion	(...) Oxides of metals.
(*v*) Hydrogenation	(...) Adsorption of hydrogen.
(*vi*) Hydride	(...) Substance which removes oxygen from other compounds.
(*vii*) Reducing agent	(...) Oxides of non-metals.
(*viii*) Claude's process	(...) Discovery of hydrogen peroxide.
(*ix*) Bosch Process	(...) Manufacture of hydrogen.
(*x*) Acid anhydrides	(...) Manufacture of oxygen.
(*xi*) Basic anhydride	(...) Sodium peroxide mixed with 1% iron oxide and 0·68% copper sulphate.
(*xii*) L. J. Thenard	(...) Compounds of metals with hydrogen.
(*xiii*) Hydrolith	(...) Conversion of oils into solid fat.

Completion Test

8. Fill in the blanks with a correct word or words in the following statements :

(i) The basis of modern periodic classification is that the properties of elements are a periodic function of their......

(ii) The vertical columns in Mendeleeff's periodic table are called...... These are ...in all. The horizontal rows are called ....

(iii) Chlorine is manufactured by the electrolysis of......

(iv) The bleaching action of chlorine is due to its reaction with.... and formation of.....

(v) The most reactive member in the halogen family is......

(vi) Hydrochloric acid gas is dried by passing it through......

(vii) Aqua regia is a mixture of......part(s) of......and...... part(s) of......

(viii) On heating a mixture of solid chloride and solid potassium dichromate with concentrated sulphuric acid......is formed.

(ix) Bleaching powder is prepared by the action of......on......

(x) The Hasenclever plant for the manufacture of bleaching powder works on the principle of......

Selection Test

9. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(i) The modern periodic table is based on the researches of (a) Newlands, (b) Mendeleeff, (c) Moseley.

(ii) Chlorine is liberated from hydrochloric acid by reacting it with (a) a reducing agent, (b) a salt, (c) an oxidising agent.

(iii) The valency of the halogen is (a) 1, (b) 2, (c) 3.

[illegible]

with water.

(v) An antichlor is a compound which (a) liberates chlorine from bleaching powder, (b) absorbs chlorine, (c) converts it into hydrochloric acid.

(vi) Silver chloride is soluble in (a) a water, (b) nitric acid, (c) ammonium hydroxide.

(vii) Halogens are placed in the modern periodic table (a) in group VIIA, (b) group VIIB, (c) group VIII.

(viii) Potassium chlorate is formed when chlorine is passed through (a) cold, (b) hot, (c) dilute solution of potassium hydroxide.

True-False Test

10. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements :

(i) In each short period the valency with respect to hydrogen increases from *one to seven.*

(ii) *Valency* of an element is known from its position in the periodic table.

(iii) Chlorine turns starch iodide paper *blue.*

(iv) Hydrochloric acid gas may be dried by passing it through *phosphorus pentoxide.*

(v) Hydrochloric acid gas is *heavier* than air.

(vi) In case a metal gives two chlorides, hydrochloric acid forms the *higher* one.

(vii) When bleaching powder is treated with *carbon dioxide,* chlorine is liberated.

(viii) *Chlorine* is used for bleaching silk.

11. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the following statements :

(i) Elements of *first short period* are called typical elements.

(ii) According to modern periodic law properties of elements are a *periodic function of their atomic weights.*

(iii) Chemically iodine is *most reactive* and fluorine is *least reactive.*

(iv) Aqua regia is a mixture of *3 parts* of concentrated hydrochloric acid and *one part* of concentrated nitric acid.

(v) Sulphur dioxide reacts with chlorine in sunlight to form *sulphuric acid.*

Matching Test

12. Mark each item in list II with appropriate numbers—(i), (ii), (iii) etc. so that it becomes related with the corresponding items in list I.

List I	List II
(i) Metalloids	(...) Law of Octaves.
(ii) Dobereiner	(...) Elements having atomic numbers from 93 to 105.
(iii) Newlands	(...) Atomic numbers.
(iv) Moseley	(...) Manufacture of chlorine.
(v) Trans-uranium elements	(...) Alkali metals.
(vi) Nelson cell	(...) Triads.

(*vii*) Group IA (...) Elements having characteristics of both metals and non-metals.

Completion test

13. Fill in the blanks with a correct word or words in the following statements :

(*i*) Block sulphur is purified by......and the vapours of sulphur, which condense on the walls, are known as......

(*ii*) Sulphur dissolves in caustic potash on heating to give .. ...and.... .

(*iii*) Sulphur dioxide is prepared in the laboratory by heating ......with .....It may also be obtained by the action of dilute sulphuric acid on. .. or . ...

(*iv*) Sulphur dioxide turns .....green.

(*v*) Sulphur trioxide combines with hydrochloric acid to give..... of which the formula is ...

(*vi*) . ....act as a catalyst in the manufacture of. .. .by the Lead Chamber Process.

(*vii*) The conditions favouring the oxidation of sulphur dioxide to ... in the Contact Process are (*a*) . , (*b*) . , (*c*) ....., (*d*) ......

(*viii*) Sulphuric acid reacts with benzene to give .. .

(*ix*) Alums may be represented by the general formula .. .

(*x*) A continuous supply of hydrogen sulphide is obtained by the action of ... on . .. in a . apparatus.

(*xi*) When hydrogen sulphide is passed through a solution of antimony chloride. . is precipitated the colour of which is.. . .

(*xii*) Carbon disulphide is manufactured by passing over . ...

14. Fill in the blanks with correct word or words in the following statements :

(*i*) Sulphur dissolves in caustic soda solution on heating to produce.. .. and .. ..

(*ii*) The chief impurities in chamber acid are , and ....

(*iii*) Sulphur dioxide dissolves in water to produce

(*iv*) Bleaching action of sulphur dioxide is due to . .. of colouring matter to a colourless product.

(*v*) Changing potassium dichromate paper green exhibits ... property of gas.

(*vi*) Reaction with hydrogen sulphide exhibits property of sulphur dioxide.

(*vii*) Sulphur trioxide dissolves in concentrated sulphuric acid and gives .....having the formula. .

(*viii*) Sulphuric acid is used in the manufacture of fertilizers, *e.g.*,......and......

(*ix*) Sulphur dioxide......hydrogen sulphide to sulphur. It ...... nitric acid and forms reddish brown fumes of......

(*x*) Sulphur is used during the process of......of rubber.

True-False Test

15. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements :

(*i*) Sulphur reduces hot nitric acid to *nitrogen dioxide.*

(*ii*) Plastic sulphur is *soluble* in carbon disulphide.

(*iii*) Rhombic sulphur is *soluble* in carbon disulphide.

(*iv*) Sulphur dioxide is an *unsaturated compound* and give *addition products.*

(*v*) Sulphur dioxide possesses *oxidising property.*

(*vi*) Nowadays *vanadium pentoxide* is used as catalyst i the manufacture of sulphuric acid by Contact Process.

(*vii*) *Concentrated sulphuric acid* is used for drying hydroge sulphide.

(*viii*) Hydrogen sulphide is *incombustible.*

(*ix*) Carbon disulphide dissolves *rubber.*

Selection Test

16. In the following statements put √ mark on the mos suitable word or expression out of the various possible alternative suggested therein :

(*i*) Monoclinic sulphur is obtained by (*a*) condensing th vapours of sulphur, (*b*) cooling the molten sulphur and pourin out the liquid by making two holes in the crust, (*c*) evaporatin solution of sulphur in carbon disulphide.

(*ii*) The most stable variety of sulphur at ordinary tempera ture is (*a*) Rhombic, (*b*) Prismatic, (*c*) Plastic.

(*iii*) A crystal of monoclinic sulphur is (*a*) cubic, (*b*) needle shaped, (*c*) octahedral.

(*iv*) The solution of sulphur dioxide in water contains (*a*) hy drogen ions, (*b*) sulphate ions. (*c*) sulphide ions.

(*v*) In the formation of sulphur dioxide by heating sulphuri acid with sulphur, the acid is (*a*) oxidized, (*b*) reduced, (*c*) neutra lized.

(*vi*) Bleaching action of sulphur dioxide is due to (*a*) reduc tion, (*b*) oxidation, (*c*) decomposition—of the colouring matter.

(*vii*) Function of Gay-Lussac's tower is (*a*) recovery of oxide of nitrogen, (*b*) denitration of nitrated acid, (*c*) concentration o dilute acid.

(*viii*) Hydrogen is liberated by the action of sulphuric acid o (*a*) iron, (*b*) copper, (*c*) silver.

(*ix*) Hydrogen sulphide is (*a*) insoluble, (*b*) fairly soluble, (*c*) extremely soluble in water.

(*x*) *When tin is heated in hydrogen sulphide, there is* (*a*) an increase, (*b*) a decrease, (*c*) no change—in the volume.

Completion Test

17. Fill in the blanks with a correct word or words in the following statements :

(*i*) Nitrogen can be prepared in the laboratory by heating a mixture of..... and......

(*ii*) Nitrogen combines with calcium carbide to form ..... mixture of......and .....

(*iii*) Ammonia is prepared in the laboratory by heating a mixture of......and......

(*iv*) In the Haber's process for the manufacture of ammonia, ...is used as catalyst and......as promoter.

(*v*) The..... colour of commercial nitric acid is due to the presence of dissolved......

(*vi*) When air is blown into an electric arc,......is formed. It is oxidised to......which dissolves in water in presence of...... to give nitric acid.

(*vii*) At 800°C, air oxidises ammonia in presence of .....which acts as a catalyst.

(*viii*) Nitric acid produces......stains on wood or skin due to the formation of......

(*ix*) Phosphorus is manufactured by heating a mixture of......, ...and......in an electric furnace.

(*x*) On heating phosphorus with caustic soda solution,...... gas is evolved.

18. Fill in the blanks with correct word or words in the following statements :

(*i*) The percentage of......is more in the air dissolved in water than in the atmosphere.

(*ii*) Ammonia may be oxidised to... . as well as... ..

(*iii*) When ammonia is passed over heated sodium at 300°C ......and..... are formed.

(*iv*) White phosphorus is soluble in... .

(*v*) ......convert atmospheric nitrogen into compounds which the plants can readily assimilate.

(*vi*) Ammonia is dried by passing the gas through

(*vii*) Elementary nitrogen present in the atmosphere is called ......nitrogen.

(*viii*) Combined nitrogen present in various nitrogenous compounds is called.... .nitrogen.

(*ix*) Conversion of......atmospheric nitrogen into......nitrogen is called......of nitrogen.

(*x*) Series of changes going on in nature which keep the percentage of nitrogen in the atmosphere practically constant are termed nitrogen......

(*xi*) In the volcano experiment......on heating leaves a green mass.

Selection Test

19. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) Nitrogen does not form nitride with (*a*) aluminium, (*b*) silver, (*c*) magnesium.

(*ii*) By 'fixation of nitrogen' is meant (*a*) manufacture of nitrogen from air, (*b*) liquefaction of nitrogen, (*c*) conversion of atmospheric nitrogen into nitrogen compounds.

(*iii*) Ammonia is (*a*) acidic, (*b*) basic, (*c*) neutral.

(*iv*) A solution of ammonia (*a*) does not contain any ions, (*b*) contains hydrogen ions, (*c*) contains hydroxyl ions.

(*v*) Fuming nitric acid contains dissolved, (*a*) nitrogen dioxide, (*b*) nitric oxide, (*c*) nitric acid vapours in excess.

(*vi*) Hydrogen is liberated by the action of very dilute nitric acid on (*a*) magnesium, (*b*) aluminium, (*c*) copper.

(*vii*) Ammonium nitrate is not produced by the action of very dilute nitric acid on (*a*) zinc, (*b*) tin, (*c*) mercury.

(*viii*) In the action of nitric acid on metals, the evolution of nitrogen dioxide is favoured by (*a*) concentrated acid, (*b*) moderately strong acid, (*c*) dilute acid.

(*ix*) Nitric acid oxidises hydrogen sulphide to (*a*) sulphur dioxide, (*b*) sulphur, (*c*) sulphuric acid.

(*x*) The formula of phosphorus is (*a*) P, (*b*) P_2, (*c*) P_4.

Matching Test

20. Mark each item in list II with appropriate numbers—(*i*), (*ii*), (*iii*), etc., so that it becomes related with the corresponding items in list I.

List I	List II
(*i*) Birkland-Eyde Process	(...) Detection of ammonia.
(*ii*) Ostwald's Process	(...) Manufacture of nitric acid from air.
(*iii*) Symbiotic bacteria	(...) Ammonia as a by-product.
(*iv*) Nessler's solution	(...) Mixture of nitroglycerine and gun cotton.
(*v*) Nitration	(...) Oxidation of ammonia to nitric acid.

(*vi*) Smokeless powder	(...) Calcium phosphate.
(*vii*) Blasting gelatine	(...) Replacement of hydrogen atom(s) by nitro group(s)—NO_2.
(*viii*) Bone-ash	(...) Conversion of nitrogen into nitrogenous compound by plants.
(*ix*) Serpek's Process	(...) Mixture of nitroglycerine, gun cotton and vaseline.

Completion Test

21. Fill in the blanks with correct word or words in the following statements :

(*i*) Graphite is manufactured by heating......or......with...... in (a, an)......

(*ii*) *Carbon monoxide is prepared in the laboratory by* heating......with......The resulting gas is passed through......which absorbs......and carbon monoxide passed on.

(*iii*) On passing carbon monoxide over heated nickel......is formed which decomposes at higher temperature to give......and...

(*iv*) Carbon dioxide is obtained as a by-product during the manufacture of......by......of sugar.

(*v*) Water gas is a mixture of......and......

(*vi*) Producer gas is a mixture of......and.... .

(*vii*) The process of breaking up of higher hydrocarbons into simpler ones is called......

True-False Test

22. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements:

(*i*) Diamonds are *good* conductors of heat and electricity.

(*ii*) Graphite is a *good* conductor of heat and electricity.

(*iii*) Graphite is used as a *lubricant*.

(*iv*) Carbon monoxide is a *saturated* compound.

(*v*) The name of the red colouring matter of blood is *haemoglobin*.

(*vi*) Fire can be prevented by cooling the burning object below its ignition temperature.

(*vii*) Pressure of the gas *affects* the luminosity of the flame.

Selection Test

23. In the following statements put ✓ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) Of the many varieties of coal, the one richest in carbon is (*a*) lignite, (*b*) bituminous, (*c*) anthracite.

(*ii*) One of the crystalline varieties of carbon is (*a*) coke, (*b*) graphite, (*c*) gas carbon.

(*iii*) Carbon monoxide is (*a*) acidic, (*b*) basic, (*c*) neutral towards litmus.

(*iv*) Carbon monoxide is (*a*) combustible, (*b*) supporter of combustion, (*c*) neither combustible nor supporter of combustion.

(*v*) Carbon monoxide is absorbed by (*a*) water, (*b*) ammonia, (*c*) ammoniacal solution of cuprous chloride.

(*vi*) Carbogen is a mixture of 5—10 per cent carbon dioxide with (*a*) oxygen, (*b*) nitrogen, (*c*) hydrogen.

(*vii*) Chemically, phosgene is (*a*) phosphorus trichloride, (*b*) carbonyl chloride, (*c*) phosphine.

Matching Test

24. Mark each item in list II with appropriate numbers—(*i*), (*ii*), (*iii*), so that it becomes related with the corresponding items in list I :

List I	List II
(*i*) Peat	(...) Mixture of carbon monoxide and hydrogen.
(*ii*) Coke	(...) Mixture of carbon monoxide and nitrogen.
(*iii*) Carborundum	(...) Mixture of carbon dioxide and oxygen.
(*iv*) Water gas	(...) Solid carbon dioxide.
(*v*) Dry ice	(...) Process of breaking of higher hydrocarbons into simpler ones.
(*vi*) Photosynthesis	(...) A variety of coal.
(*vii*) Carbogen	(...) Silicon carbide.
(*viii*) Producer gas	(...) Coal—volatile matter.
(*ix*) Cracking	(...) Plants prepare food from carbon di in the presence o chlorophyll.

KEY TO THE SOLUTIONS

1. (*i*) Sodium peroxide ; (*ii*) nitrogen, volati lysis, action of metals, action of hydrides ; (*iv*) ste red hot iron; (*v*) pure HCl, magnesium; (*vi*) bases, ble salts of calcium and magnesium ; (*viii*) adding sulphuric acid, carbon dioxide ; (*x*) alumina, silica,

2. (*i*) 21 ; 50 ; (*ii*) Combustion ; (*iii*) Adsorp (*iv*) Ammonia, methanol, petrol substitutes, va (*v*) Oxygen, electronegative ; hydrogen ; electroposi dation-reduction or redox.

3. (*i*) T, (*ii*) T, (*iii*) F—only at the surface, (*iv*) F—nickel, (*v*) T, (*vi*) F—sodium chloride, (*vii*) T, (*viii*) T.

4. (*i*) T, (*ii*) T, (*iii*) T, (*iv*) F—bases, basic anhydrides.

5. (*i*) *a*, (*ii*) *b*, (*iii*) *b*, (*iv*) *a*, (*v*) *a*, (*vi*) *c*, (*vii*) *b*.

6. (*i*) *b*, (*ii*) *a*. (*iii*) *b*, (*iv*) *b*, (*v*) *c*.

7. (*iii*), (*i*), (*xiii*), (*xi*), (*iv*), (*vii*), (*x*), (*xii*), (*ix*), (*viii*), (*ii*), (*vi*), (*v*).

8. [illegible]
(*iv*) wa [illegible]
(*vii*) th [illegible]
(*ix*) chlorine, slaked lime ; (*x*) counter-currents.

9. (*i*) *c*, (*ii*) *c*, (*iii*) *a*, (*iv*) *c*, (*v*) *c*, (*vi*) *c*, (*vii*) *a*, (*viii*) *b*.

10. (*i*) F—one to four and then decrease from four to one, (*ii*) T, (*iii*) T, (*iv*) F—conc. sulphuric acid, (*v*) T, (*vi*) F—lower, (*vii*) T, (*viii*) F—sulphur dioxide.

11. (*i*) F—second short period. (*ii*) F—atomic numbers.
(*iii*) F—least reactive ; most reactive.
(*iv*) T. (*v*) F—sulphuryl chloride.

12. (*iii*), (*v*), (*iv*), (*vi*), (*vii*), (*ii*), (*i*).

13. (*i*) Distillation, flowers of sulphur.
(*ii*) Sulphide, thiosulphate.
(*iii*) Copper, conc. sulphuric acid, sulphite, bisulphite.
(*iv*) Acidified potassium dichromate solution.
(*v*) Chloro-sulphonic acid, $Cl.SO_2.OH$.
(*vi*) Oxides of nitrogen, sulphuric acid.
(*vii*) Sulphur trioxide, (*a*) low temperature, (*b*) high pressure, (*c*) excess of air, (*d*) catalyst.
(*viii*) Benzenesulphonic acid.
(*ix*) $X_2SO_4.Y_2(SO_4)_3.24H_2O$.
(*x*) Dil. sulphuric acid, iron sulphide, Kipp's.
(*xi*) Antimony sulphide, orange.
(*xii*) Sulphur vapours, red hot coke.

14. (*i*) Sodium sulphide ; sodium thiosulphate.
(*ii*) Arsenious oxide ; lead sulphate ; oxides of nitrogen.
(*iii*) Sulphurous acid.
(*iv*) Reduction. (*v*) Reducing.
(*vi*) Oxidising. (*vii*) Oleum ; $H_2S_2O_7$.
(*viii*) Ammonium sulphate ; superphosphate of lime.
(*ix*) Oxidises ; reduces ; nitrogen dioxide.
(*x*) Vulcanization.

15. (*i*) T, (*ii*) F—insoluble, (*iii*) T, (*iv*) T, (*v*) T, (*vi*) T, (*vii*) F—Calcium chloride or phosphorus pentoxide, (*viii*) F—combustible, (*ix*) T.

16. (*i*) *b*, (*ii*) *a*, (*iii*) *b*, (*iv*) *a*, (*v*) *b*, (*vi*) *a*, (*vii*) *a*, (*viii*) *a*, (*ix*) *b*, (*x*) *c*.

17. (*i*) Sodium nitrite ; ammonium chloride ; (*ii*) nitrolim, carbon, calcium cyanamide ; (*iii*) ammonium chloride, slaked lime ; (*iv*) finely-divided iron, molybdenum ; (*v*) yellow, nitrogen dioxide ; (*vi*) nitric oxide, nitrogen dioxide, air ; (*vii*) platinum gauze ; (*viii*) yellow, nitrocellulose ; (*ix*) bone-ash, coke, silica ; (*x*) phosphine.

18. (*i*) Oxygen ; (*ii*) nitrogen, nitric oxide ; (*iii*) Sodamide, hydrogen ; (*iv*) carbon disulphide ; (*v*) symbiotic bacteria ; (*vi*) quick-lime ; (*vii*) free ; (*viii*) fixed ; (*ix*) free, fixed, fixation ; (*x*) cycle ; (*xi*) ammonium dichromate.

19. (*i*) *b*, (*ii*) *c*, (*iii*) *b*, (*iv*) *c*, (*v*) *a*, (*vi*) *a*, (*vii*) *c*, (*viii*) *a*, (*ix*) *b*, (*x*) *c*.

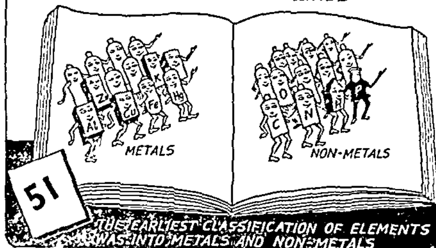
20. (*iv*), (*i*), (*ix*), (*vii*), (*ii*), (*viii*), (*v*), (*iii*), (*vi*).

21. (*i*) anthracite, coke, silica, electric furnace ; (*ii*) oxalic acid, conc. sulphuric acid, caustic soda, carbon dioxide ; (*iii*) nickel carbonyl, nickel, carbon monoxide ; (*iv*) alcohol, fermentation ; (*v*) carbon monoxide, hydrogen ; (*vi*) carbon monoxide, nitrogen ; (*vii*) cracking.

22. (*i*) F, bad, (*ii*) T, (*iii*) T, (*iv*) F, unsaturated, (*v*) T, (*vi*) T, (*vii*) T.

23. (*i*) *c*, (*ii*) *b*, (*iii*) *c*, (*iv*) *a*, (*v*) *c*, (*vi*) *a*, (*vii*) *b*.

24. (*iv*), (*viii*), (*vii*), (*v*), (*ix*), (*i*), (*iii*), (*ii*), (*vi*).



Metals and Metallurgy

1. Classification of Elements as Metals and Non-metals.— The primary object of classification is to so arrange the known facts that we may learn the maximum possible of them with the least possible effort. The earliest classification of the elements was into metals and non-metals. Originally the classification was based on the physical properties of the elements but the one based on chemical grounds is found to be more satisfactory.

It will be seen from the properties of metals and non-metals given in the table below that there is no sharp line of division between metals and non-metals. The two classes of elements are found to merge into each other so often that exact sub-division is not practicable. In spite of all this classification of elements into metals and non-metals is often a convenient one.

Metals	Non-metals
1. State. Metals are solids at ordinary temperature and volatilize only at high temperatures. *Exception* : Mercury is a liquid.	1. These are either gases at ordinary temperatures or liquids and solids which volatilize at low temperatures. *Exceptions* . Carbon, boron, and silicon.
2. Lustre. Most metals are shining in appearance and take a high polish.	2 Non-metals possess no metallic lustre. *Exceptions* Graphite and iodine
3. Hardness. Metals are generally hard and their alloys are harder. *Exceptions* : Alkali metals are waxy solids.	3 Hardness varies Diamond is the hardest substance known

Metals	Non-metals
4. Malleability*, Ductility and Tenacity.** Metals are generally malleable, ductile and tenacious. *Exceptions :* Arsenic, antimony and bismuth.	4. Non-metals possess no malleability, ductility or tenacity.
5. Density*** Specific gravity of metals is generally high. *Exceptions* : Light metals, lithium, sodium, potassium, etc.	5. Their specific gravity is generally low.
6. Conductivity.**** Metals are generally good conductors of heat and electricity and electrical resistance usually increases with rise of temperature. *Exception* : Bismuth is not a very good conductor.	6. Non-metals are generally poor conductors of heat and electricity and electrical resistance usually decreases with rise of temperature. *Exceptions :* Graphite and gas carbon.
7. Atomicity. Molecules of metals in the vapour state are usually monoatomic.	7. Non-metals in vapour state contain poly-atomic molecules usually.
8. Alloy formation. Metals form homogeneous mixtures, alloys with other metals.	8. Non-metals do not form alloys. *Exceptions* : Carbon, silicon and phosphorus which form alloys with metals.
9. Nature of oxides. Metals form basic oxides. *Exceptions* : CrO_3, Mn_2O_7 are acidic ; Al_2O_3, ZnO, SnO_2 are amphoteric.	9. Non-metals form acidic oxides.
10. Hydrides. Metallic hydrides are either not formed at all or are very unstable.	10. Hydrides of non-metals are quite stable.
11. Electropositive nature. Metals form cations in solution and are deposited on the cathode during electrolysis, *i.e.*, these are electropositive in character. $NaCl \rightleftharpoons Na^+ + Cl^-$	11. Electronegative nature. Non-metals form anions in solution and are deposited on the anode during electrolysis, *i.e.*, these are electronegative in character. $KBr \rightleftharpoons K^+ + Br^-$

*Malleability is the property of the metals of being beaten into thin sheets. Metals arranged in the order of decreasing malleability are :

Au ; Ag ; Cu ; Sn ; Pt ; Pb ; Zn ; Fe ; Ni.

**Tenacity of a metal is measured by the weight which its wire (1 sq. inch cross-section) can support. Metals arranged in the order of their decreasing tenacity are : Fe (62) ; Cu ; Pt ; Ag ; Au ; Al (20) ; Zn ; Pb (2).

***Density is mass per unit volume. Metals arranged in the order of decreasing density are : Pt (21·4) ; Au (19·26) ; Hg (13·6) ; Pb (11·3) ; Ag (10·5) ; Cu (8·95) ; Fe (7·8) ; Zn (6·86) ; Na (0·97) ; K (0·86).

****Conductivity. Metals arranaged in the order of decreasing conductivity are : Ag (60) ; Cu (56) ; Au (41) ; Al (34) ; Zn (16) ; Pt (9) ; Fe (8·3) ; Hg (1·05).

Metals	Non-Metals
Exceptions : Chromium and manganese form anions also, *e.g.*, in chromate (CrO_4^{2-}) and manganate (MnO_4^{2-}).	*Exception* : Hydrogen.
12. Solubility. Metals do not dissolve except by chemical reaction. For example, sodium dissolves in water and iron in sulphuric acid. $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$ $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2\uparrow$	12. Non-metals are soluble even without chemical reactions. For example, chlorine is soluble in water, phosphorus in carbon disulphide.
13. Action of acids. Metals dissolve in mineral acids with the evolution of gas and forming corresponding salts. $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$ $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$ $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$	13. Non-metals either do not react at all or form corresponding oxy-acids with acids. $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$

2. Metallic Bonding.— A molten metal solidifies to produce a crystalline structure, which has a high melting point, high tensile strength and is a good conductor of heat and electricity. The units are held within a metallic crystal by metallic bonding, which may be described as follows .

(1) The valency electrons in a metal are not strongly held by the atoms (low ionization energy).

(2) The atomic orbitals holding the valency electrons are assumed to merge to produce a delocalized orbital system throughout which the electrons are free to move and this permeates the whole metal lattice.

(3) Conductivity of metals is due to the freedom of the valency electrons to move in the delocalised system under the influence of potential gradient. As electrons flow, a current is set up.

(4) The structural units of a metallic crystal are atoms which have been deprived of their valency electrons (these having entered the delocalised orbital). These units cannot properly be called cations, since (i) no anions are present, and (ii) the electrons in the delocalised system are still associated with the atoms fairly closely.

The name *atomic core* has been suggested to denote that the unit is a type of cation, in which the charge transfer is less complete than that between a cation and an anion.

(5) A metal crystal is, therefore, a close-packed assembly of atomic cores (positively charged) surrounded by an electron flux.

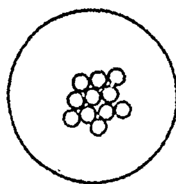


Fig. 51·1—Close-packed spheres in a watch glass.

Place a number of glass spheres on a watch glass which is gently shaken. As a crude analogy, the spheres represent the atomic cores, while the attractive force of the electron flux may be compared to the force of gravity on the spheres due to the concave surface of watch glass.

(6) The strength of the metal bonding system increases with :

(*a*) an increase in the number of electrons in the delocalised system, and

(*b*) a decrease in the size of the atomic core which forms the structural unit.

For example—

(*i*) The alkali metals, which form large cations, have only one electron which is available to enter the delocalized system. The strength of the metallic bond is low, and these metals have low melting points and are soft, malleable and ductile.

(*ii*) Transition metals form small cations, and can release quite a number of electrons into the metallic bond, so that these metals are hard, with a high tensile strength and have high melting points, corresponding to a strong metallic bonding system.

3. **Metalloids.**—We come across some borderline cases among the elements. They behave like metals under some circumstances and act like non-metals under different conditions. These are called *metalloids*. For example, arsenic has a metallic appearance, is a conductor of electricity and forms alloys. Thus from a physical point of view it would be reckoned as a metal. Arsenious sulphide, As_2S_3 precipitated by passing hydrogen sulphide through any arsenic salt solution is similar to sulphides of copper, mercury, etc.

On the contrary, both of its oxides (As_4O_6 and As_4O_{10}) are acidic in nature and form salts, the arsenites and arsenates (*cf.*, P_4O_6 and P_4O_{10} which form phosphites and phospates). Its hydride, arsine (AsH_3) is quite stable whereas its chloride is easily hydrolysed. It is oxidised by concentrated nitric acid to its highest oxy-acid, arsenic acid, H_3AsO_4. Thus from its chemical behaviour, it is a non-metal. Arsenic is, therefore, a borderline case and is said to be a metalloid. Antimony also exhibits the properties of both metals and non-metals and is a metalloid.

4. **Alloys.**—A homogeneous mixture of a metal with another metal or a non-metal is called an *alloy*. It is a type of solid solution or a definite compound of its constituent elements.

Preparation of Alloys. Common methods used for the preparation of various alloys are :

(*i*) **Fusion.** The various components are taken in proper proportion, melted and stirred with charcoal pieces.

(*ii*) **Compression.** Some alloys, *e.g.*, wood's metal, are obtained by mechanically compressing the various constituents taken in proper proportion.

(*iii*) **Electrodeposition.** In some cases an alloy is obtained by simultaneous electrodeposition of its components from a solution containing both. Brass can be prepared in this way.

Properties of Alloys. The properties of alloys vary greatly with their composition. Their hardness is generally greater while malleability or ductility is less than that of their components. The ... ally lower than the melting points ... alloy usually resists corrosion. It ... machined easily.

Pretty large number of alloys have so far been prepared. These are prepared with the following ends in view :

(*i*) To increase hardness, *e.g.*, gold becomes harder by alloying copper with it.

(*ii*) To make them more resistant to corrosion, *e.g.*, stainless steel (alloy or iron and chromium) is acid proof and rust proof.

(*iii*) To increase tensile strength, *e.g.*, chrome vanadium steel.

(*iv*) To lower melting point, *e.g.*, fusible alloys.

(*v*) To modify colour, *e.g.*, aluminium bronze is beautiful golden.

(*vi*) To modify chemical activity, *e.g.*, sodium amalgam.

(*vii*) To get good castings, *e.g.*, type metal.

Classification of Alloys. Alloys have been classified as—

(*a*) **Ferrous Alloys.** Alloys containing iron as one of the constituents are called *ferrous alloys*, *e.g.*, alloy steels.

(*b*) **Non-ferrous Alloys.** Alloys other than the ferrous alloys are called *non-ferrous alloys.*

(*c*) **Amalgams.** Alloys of mercury with other metals are called *amalgams*, *e.g.*, sodium amalgam, zinc amalgam

For composition and uses of important alloys see individual metals.

5. **Occurrence of Metals.**—Very few metals occur in the element form, *i.e.*, native ; most of them occur as their compounds associated with sandy matter and other impurities in the earth's crust. *The various compounds of metals which occur in nature are called* **minerals.**

Those minerals from which the metal can be profitably extracted are called ores. So all ores are minerals but all minerals are not ores. Thus metals occur in nature—

(*i*) *Free or native.* For example, gold, platinum, silver and copper are found native.

(*ii*) *As Oxides.* For example, cuprite, Cu_2O ; zincite, ZnO ; bauxite, $Al_2O_3.2H_2O$ and haematite, Fe_2O_3.

(*iii*) *As Sulphides.* For example, copper pyrites, $CuFeS_2$; argentite, Ag_2S ; zinc blende, ZnS ; cinnabar, HgS and galena, PbS.

(*iv*) *As Carbonates.* For example, malachite, $CuCO_3.Cu(OH)_2$; limestone, $CaCO_3$; dolomite, $MgCO_3.CaCO_3$; calamine, $ZnCO_3$ and siderite $FeCO_3$.

(*v*) *As Sulphates.* For example, barium and lead occur as barytes, $BaSO_4$ and anglesite, $PbSO_4$, respectively.

(*vi*) *As Silicates.* For example, hemimorphite $2ZnO.SiO_2.H_2O$ is an ore of zinc.

(*vii*) *As Halides.* For example, sodium chloride, NaCl and horn silver, AgCl.

6. **Mineral Wealth of India.**—India is quite fortunate to have been gifted by nature with rich mineral resources. For example :

(*i*) **Iron** occurs as haematite, Fe_2O_3 in Bihar, Orissa and Madhya Pradesh. Clay iron ore is found in Mysore.

(*ii*) **Coal** is available in large quantities in close proximity to iron.

(*iii*) **Manganese.** Next to Russia we are the biggest producers of manganese. Manganese ore is found in Madhya Pradesh, Maharashtra, Andhra Pradesh, Bihar, Orissa, Rajasthan, Tamil Nadu, Mysore and Gujarat.

(*iv*) **Copper** occurs in Bihar, Orissa, Mysore and Sikkim.

(*v*) **Gold** is found in free state in Mysore, Hyderabad and in the alluvial sands of the Ganges, the Brahmaputra and the Irrawady.

(*vi*) **Aluminium.** Bauxite, an ore of aluminium, is available in Madhya Pradesh, Bihar, Orissa, Salem (Tamil Nadu), Saurashtra, Kutch and Kashmir States.

(*vii*) **Tin** occurs as tinstone in Bihar, Orissa and Rajasthan.

(*viii*) **Chromium** is found as chrome iron ore in Bihar, Orissa, Maharashtra and Mysore.

(*ix*) **Limestone** is available in Satna, Katni and Rohtasgarh. Marble is found in Jaipur and Madhya Pradesh.

(*x*) **Mica.** India is the chief producer of mica. It occurs in Bihar, Orissa, Tamil Nadu and Rajasthan.

(*xi*) **Monazite.** It is the costly thorium ore (£ 2,000 per ton) which occurs in Travancore and India has the sole monopoly for it.

Estimates of Mineral Production (in thousand tonnes) in India

	Year	1960-61	1965-66*	1970-71	1975-76
1.	Coal	52,593	89 000	140,000	210,000
2.	Iron ore	10,683	27,000	60,000	90,000
3.	Manganese ore	1,199	2,100	3,000	3,900
4.	Limestone	15,993	27,500	52,000	82,000
5.	Copper ore	448	990	4,900	8,000
6.	Chromite	100	90	190	270
7.	Bauxite	387	920	2,500	4,000
8.	Gold (in kg)	4,995	5,000	5,000	5,000
9.	Mica	29	32	42	50
10.	Salt	3,950	5,200	7,300	10,500
11.	China Clay	353	700	1,250	1,900
12.	Dolomite	650	1,200	3,600	7,000

7. Metallurgy.—The branch of science dealing with the methods of extraction of metals from their ores and the *preparation of alloys is called metallurgy.*

The metallurgy of each metal is an individual problem and the line of treatment depends upon the nature of ore and the chemical properties of the metal. Thus the problem is partly physical and partly chemical. Different metallurgical operations employed in extracting metals from their ores in general are given below :

(1) **Concentration.** The ores are mostly obtained from the ground and contain large quantities of foreign materials as impurity. *The unwanted impurities, e g., earthy particles, rocky matter, sand, limestone, etc., present in an ore, are called* gangue or matrix.

The process of removal of gangue from powdered ore is technically known as concentration.

For concentration the ore is crushed to the suitable size in big jaw crushers, and ... mills or stamp battery followed ... the concentration of the finely powdered ore is carried out in one or more of the following ways :

(*i*) Gravity Separation The crushed ore is treated with a stream of water in a big *jig* (shaking machine) or on a *Wilfley table* (with corrugated top). The lighter gangue particles are washed away while heavier ore particles remain sunk at the bottom. Generally oxide ores, *e g.*, tinstone, haematite are concentrated by this method.

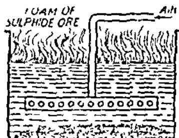


Fig 51 2—Froth Flotation Process

(*ii*) Froth Flotation Process In the case of sulphide ores advantage is taken of the preferential wetting of the ore particles by oil and of ... com- ... 2). ... in

the form of a scum which is skimmed off. Gangue particles remain sunk to the bottom. Concentration of copper pyrites, $CuFeS_2$; zinc blende, ZnS and galena, PbS is done by this very method.

(*iii*) **Electromagnetic Separation.** When either the ore or impurity happens to be magnetic in nature the two are separated by dropping the powdered ore over a travelling belt. Tinstone and wolfram (*magnetic*) are separated from each other by this method.

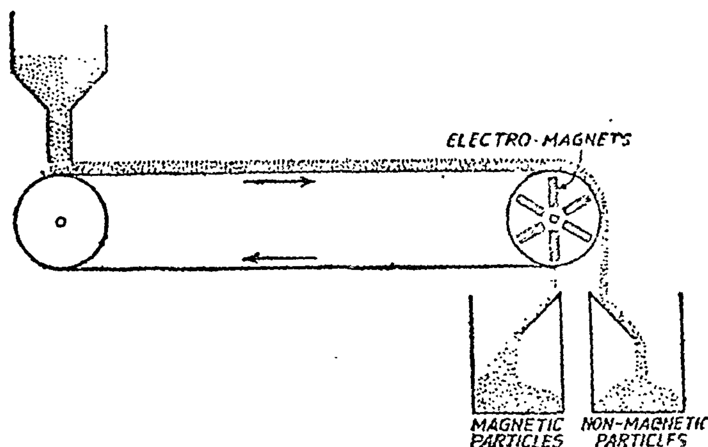
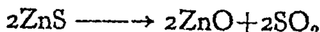


Fig. 51·3—Magnetic separation.

(2) **Working up of the Concentrated ore.** The concentrated ore is worked up by one of the following methods depending upon its nature :

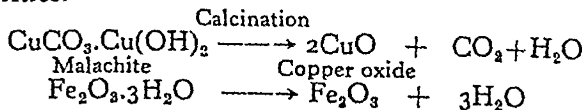
(*a*) **Smelting.** It consists in conversion of the ore into an oxide by roasting or *calcination* followed by reduction of the oxide with carbon etc. in the presence of *flux*. The flux removes the impurities present as *fusible slag* which floats on the metal and protects it from oxidation.

Roasting is the process of heating the ore strongly in excess of air. During roasting the volatile impurities are removed and the ore changed to oxide. Sulphide ores are generally roasted when they change to oxides. For example, zinc sulphide is roasted to get zinc oxide.



$$2ZnS \longrightarrow 2ZnO + 2SO_2$$

Calcination is the process of heating strongly of the ore *in absence of air*. The volatile impurities are removed and the mass becomes porous. Carbonate and oxide ores are generally calcined when they lose moisture, carbon dioxide and other volatile impurities.

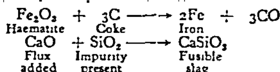


$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \xrightarrow{\text{Calcination}} \underset{\text{Copper oxide}}{2CuO} + CO_2 + H_2O$$

$$Fe_2O_3.3H_2O \longrightarrow Fe_2O_3 + 3H_2O$$

For reduction the oxide obtained by roasting or calcination of the ore is **smelted**, *i.e.*, reduced with carbon in the presence of

-an additional substance called flux. The flux combines with sandy [illegible] During reduction of haema- [illegible] with silica present as im- [illegible]



$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
Haematite, Coke, Iron

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
Flux added, Impurity present, Fusible slag

(*b*) Aluminothermic Process. Metals which are too active to be obtained by reduction of their oxides with carbon are reduced with aluminium powder, a more powerful reducing agent. Ordinarily it is not practicable to use aluminium for the preparation of metals cheaper than aluminium. Of course, small quantities of *carbon-free* metals needed for special purpose are obtained by [illegible]

This reaction is strongly exothermic and proceeds with an explosive violence. A lecture demonstration of the thermit reaction can be given as follows :

Expt. A filter paper cone is filled with thermit mixture (iron oxide + powdered aluminium) and supported in a piece of asbestos having a hole in its [illegible]

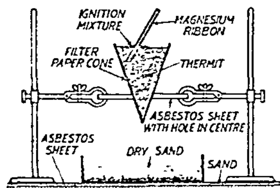
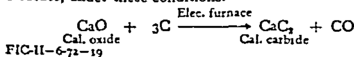


Fig. 51·4—Lecture demonstration of thermit reaction.

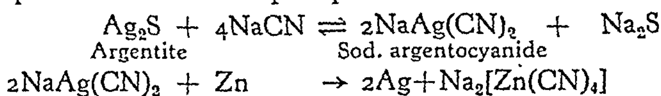
(*c*) By Electrolysis. Oxides of very active metals, *e.g.*, calcium, magnesium, aluminium and the alkali metals can be reduced with carbon only at extremely high temperatures, *e.g.*, in an electric furnace, but the metals react with carbon to form carbides, under these conditions.



$$\underset{\text{Cal. oxide}}{CaO} + 3C \xrightarrow{\text{Elec. furnace}} \underset{\text{Cal. carbide}}{CaC_2} + CO$$

Such metals can be prepared by electrolysis of their fused salts. Aqueous solutions cannot be used, as on electrolysis the metal reacts with water to give hydrogen. Thus sodium is obtained by electrolysis of fused sodium hydroxide or sodium chloride, calcium by electrolysis of fused calcium chloride and aluminium by electrolysis of alumina in fused cryolite.

(*d*) **By Metal Replacement.** Metals like gold and silver can be precipitated from their salt solutions by electropositive metal, *e.g.*, zinc. Metallic silver is dissolved from its ore in dilute sodium cyanide solution and the solution so obtained is treated with scrap zinc when silver is precipitated.



$$\underset{\text{Argentite}}{Ag_2S} + 4NaCN \rightleftharpoons \underset{\text{Sod. argentocyanide}}{2NaAg(CN)_2} + Na_2S$$

$$2NaAg(CN)_2 + Zn \rightarrow 2Ag + Na_2[Zn(CN)_4]$$

(3) **Refining.** Metals obtained above are generally impure and are refined in one or more of the following ways:

(*i*) **Poling.** The molten metal is stirred with green poles of wood. The wood gases (hydrocarbons, like methane) reduce any oxide present in the metal, *e.g.*, copper oxide present in blister copper.

In addition to this large quantities of air are sucked up when the molten metal is stirred. This oxidizes readily oxidisable impurities present in the metal. For example, on poling impurities present in block tin are oxidized and carried to the surface as scum which is removed.

(*ii*) **Liquation.** Easily fusible metals, *e.g.*, lead and tin, are heated on the sloping hearth of a reverberatory furnace. The metal melts and flows down leaving the infusible impurities, called 'dross', behind.

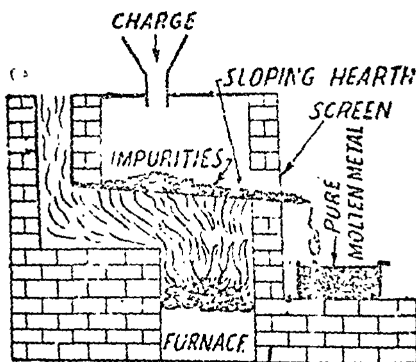


Fig. 51·5—Liquation.

(*iii*) **Distillation.** Volatile metals, *e.g.*, zinc and mercury, are freed from the non-volatile impurities by distillation.

(*iv*) **Electrolytic Refining.** The impure metal is made the anode and a thin plate of the pure metal made the cathode in an electrolytic cell containing a suitable electrolyte. On applying suitable E. M. F., the metal from the anode goes in solution and pure metal from the electrolyte is deposited on the cathode which grows in size. More electropositive metallic impurities pass into solution but are not deposited on the cathode while less electropositive impurities fall down as anodic mud and are not dissolved. Copper, silver, zinc, aluminium, tin and lead are purified electrolytically.

QUESTIONS

Essay-type Questions

1. Briefly discuss the classification of elements into metals and non-metals.

2. In what respects do metals differ from non-metals? Give a brief account of the following processes as used in the extraction of metals.

(a) Concentration ; (b) Smelting : (c) Refining.
(Delhi H.S. 1966, 63, 61 ; Punjab Pre-University 1963)

3. Give a brief account of the following processes as used in the extraction of metals :

(i) Concentration by froth flotation process.

(ii) Roasting in a reverberatory furnace.

(iii) Refining by electrolytic method and liquation.
(Punjab Pre-Univ. 1971, 70 ; Guru Nanak 1971)

4. Give an account of the important processes by which metals are prepared on a large scale. *Or*

Explain the following metallurgical terms : Malleability, Ore, Froth

tant properties of alloys ?

6. What is an alloy ? Give the methods employed for the preparation of alloys. Give the composition and use of the following alloys : (a) German silver, (b) Brass, (c) Bronze, (d) Type metal. (e) Magnalium, (f) Duralumin.
(Delhi H.S. 1961)

7. What are metalloids, alloys and amalgams ? Give two examples of each. Give reasons for the uses of alloys in preference to pure metals

8. What are metalloids ? What elements are called metalloids and why ? *(Punjab Pre-Univ. 1971)*

9. How many of the following terms can you define or explain ?

Malleability	Metalloids	Gravity separation
Ductility	Alloys	Froth flotation process
Tenacity	Amalgam	Electromagnetic process
Atomicity	Metallurgy	Aluminothermic separation
Concentration	Smelting	Electromotive series.
Flux	Slag	Poling

Test Your Understanding

10. Fill in the blanks in the following :

(a) A mineral used in the manufacture of a metal is known as ..

(b) Oxide and carbonate ores are usually concentrated by while sulphide ores are usually concentrated by ...

(c) A sulphide ore is usually roasted in order to

(d) Highly electropositive metals like alkali metals are obtained by. ....

(e) For removing silica occurring as an impurity . .is added during smelting.

(f) In electrolytic refining the impure metal is made . ...

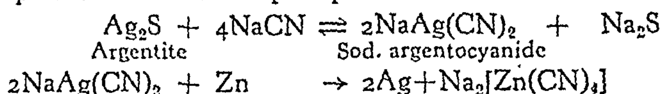
(g) Reduction of an oxide of a metal by aluminium is known as......

(h) Sodium cyanide solution is used to extract......from their ores.

(i) The usual reducing agent for metal oxides is .....

Such metals can be prepared by electrolysis of their fused salts. Aqueous solutions cannot be used, as on electrolysis the metal reacts with water to give hydrogen. Thus sodium is obtained by electrolysis of fused sodium hydroxide or sodium chloride, calcium by electrolysis of fused calcium chloride and aluminium by electrolysis of alumina in fused cryolite.

(d) **By Metal Replacement.** Metals like gold and silver can be precipitated from their salt solutions by electropositive metal, *e.g.*, zinc. Metallic silver is dissolved from its ore in dilute sodium cyanide solution and the solution so obtained is treated with scrap zinc when silver is precipitated.



$$\underset{\text{Argentite}}{Ag_2S} + 4NaCN \rightleftharpoons \underset{\text{Sod. argentocyanide}}{2NaAg(CN)_2} + Na_2S$$

$$2NaAg(CN)_2 + Zn \rightarrow 2Ag + Na_2[Zn(CN)_4]$$

(3) **Refining.** Metals obtained above are generally impure and are refined in one or more of the following ways:

(i) **Poling.** The molten metal is stirred with green poles of wood. The wood gases (hydrocarbons, like methane) reduce any oxide present in the metal, *e.g.*, copper oxide present in blister copper.

In addition to this large quantities of air are sucked up when the molten metal is stirred. This oxidizes readily oxidisable impurities present in the metal. For example, on poling impurities present in block tin are oxidized and carried to the surface as scum which is removed.

(ii) **Liquation.** Easily fusible metals, *e.g.*, lead and tin, are heated on the sloping hearth of a reverberatory furnace. The metal melts and flows down leaving the infusible impurities, called 'dross', behind.

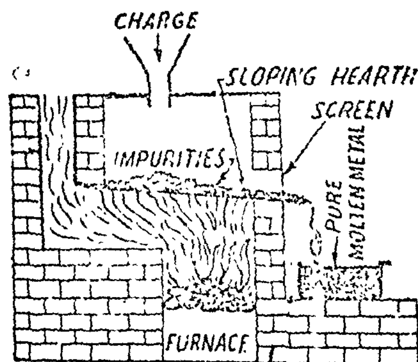


Fig. 51·5—Liquation.

(iii) **Distillation.** Volatile metals, *e.g.*, zinc and mercury, are freed from the non-volatile impurities by distillation.

(iv) **Electrolytic Refining.** The impure metal is made the anode and a thin plate of the pure metal made the cathode in an electrolytic cell containing a suitable electrolyte. On applying suitable E. M. F., the metal from the anode goes in solution and pure metal from the electrolyte is deposited on the cathode which grows in size. More electropositive metallic impurities pass into solution but are not deposited on the cathode while less electropositive impurities fall down as anodic mud and are not dissolved. Copper, silver, zinc, aluminium, tin and lead are purified electrolytically.

QUESTIONS

Essay-type Questions

1. Briefly discuss the classification of elements into metals and non-metals.

2. In what respects do metals differ from non-metals? Give a brief account of the following processes as used in the extraction of metals.

(a) Concentration ; (b) Smelting ; (c) Refining.
(Delhi H.S. 1966, 63, 61 ; Punjab Pre-University 1963)

3. Give a brief account of the following processes as used in the extraction of metals :

(i) Concentration by froth flotation process.

(ii) Roasting in a reverberatory furnace

(iii) Refining by electrolytic method and liquation.
(Punjab Pre-Univ. 1971, 70 ; Guru Nanak 1971)

4. Give an account of the important processes by which metals are prepared on a large scale. *Or*

Explain the following metallurgical terms : [illegible] flotation process, Flux, Sla[illegible]

5. What is an alloy [illegible] prepared ? What are the important properties of alloys ?

6. What is an alloy ? Give the methods employed for the preparation of alloys. Give the composition and use of the following alloys : (a) German silver, (b) Brass, (c) Bronze, (d) Type metal, (e) Magnalium, (f) Duralumin.
(Delhi H.S. 1961)

7. What are metalloids, alloys and amalgams ? Give two examples of each. Give reasons for the uses of alloys in preference to pure metals.

8. What are metalloids ? What elements are called metalloids and why ?
(Punjab Pre-Univ. 1971)

9. How many of the following terms can you define or explain ?

Malleability	Metalloids	Gravity separation
Ductility	Alloys	Froth flotation process
Tenacity	Amalgam	Electromagnetic process
Atomicity	Metallurgy	Aluminothermic separation
Concentration	Smelting	Electromotive series.
Flux	Slag	Poling

Test Your Understanding

10. Fill in the blanks in the following :

(a) A mineral used in the manufacture of a metal is known as .....

(b) Oxide and carbonate ores are usually concentrated by ... while sulphide ores are usually concentrated by

(c) A sulphide ore is usually roasted in order to......

(d) Highly electropositive metals like alkali metals are obtained by ....

(e) For removing silica occurring as an impurity......is added during smelting.

(f) In electrolytic refining the impure metal is made......

(g) Reduction of an oxide of a metal by aluminium is known as......

(h) Sodium cyanide solution is used to extract......from their ores.

(i) The usual reducing agent for metal oxides is......

11. Arrange the following according to instructions given :

(i) $KClO_4$, HCl, $KClO_3$. (in the order of increasing valency of chlorine)

(ii) $CaSO_4$, $BaSO_4$, Na_2SO_4 (in the order of decreasing solubility in water)

(iii) Al, Pb, Fe (in the order of increasing density)

(iv) $NaHCO_3$, Na_2CO_3, $CaCO_3$ (in the order of increasing thermal stability)

(v) Zn, Na, K (in the order of decreasing electropositive character)

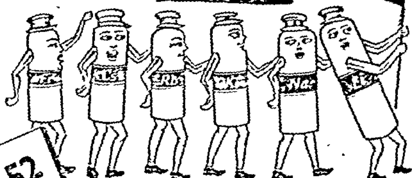
(vi) Br, I, F, Cl (in the order of increasing atomic size)

(*I.I.T. Admission Test 1970*)

KEY

10. (*a*) an ore ; (*b*) gravity process ; froth flotation process ;
(*c*) convert it into oxide of the metal ;
(*d*) electrolysis of fused chlorides ; (*e*) a basic flux like lime ;
(*f*) anode ; (*g*) aluminothermy ;
(*h*) silver and gold ; (*i*) coke.

11. (i) HCl, $KClO_3$, $KClO_4$; (*ii*) $BaSO_4$, $CaSO_4$, Na_2SO_4 ;
(*iii*) Al, Fe, Pb ; (*iv*) $NaHCO_3$, $CaCO_3$, Na_2CO_3 ;
(*v*) K, Na, Zn ; (*vi*) F, Cl, Br, I.



The Alkali Metals

... of the ... potassium ... ey con- ... own by some of their outstanding properties summarized below. This justifies their inclusion in the same sub-group of the periodic table.

(*a*) They are all silvery white, malleable and soft metals which can be easily cut. They have low melting points.

These properties indicate that the metallic bonding system is rather weak, since :

(*i*) The atoms of the alkali metals are large, and thus the structural units in the metal crystal are bulky ; hence the crystal has a low density.

(*ii*) Only one valency electron per atom enters the metallic bond.

The weak metallic bond results from a combination of these two factors ; *i.e.*, a bulky structure is held by the minimum number of binding electrons.

(*b*) They are light metals and their specific gravity increases regularly from lithium to francium while melting and boiling points decrease regularly.

(*c*) They are all monovalent and strongly electropositive. This is due to their similar electronic configuration with one valency

electron in each case as given below :

Element	At. No.	Electronic Configuration
Lithium	3	2, 1
Sodium	11	2, 8, 1
Potassium	19	2, 8, 8, 1
Rubidium	37	2, 8, 18, 8, 1
Caesium	55	2, 8, 18, 18, 8, 1
Francium	87	2, 8, 18, 32, 18, 8, 1

(*d*) They all decompose water vigorously liberating hydrogen and forming soluble bases or alkalis and hence are called the alkali metals.

(*e*) They are all very reactive and combine directly with hydrogen, oxygen, sulphur, nitrogen and carbon. For this reason they are not found free in nature.

(*f*) They are all strong reducing agents.

(*g*) Their compounds exhibit similar properties. For example :

(*i*) Oxides are strongly basic.

(*ii*) Hydroxides are strong bases, soluble in water and stable towards heat.

(*iii*) Chlorides are soluble in water and not hydrolysed.

(*iv*) Nitrates on heating give nitrites and oxygen. Lithium nitrate, which on heating gives lithium oxide and nitrogen dioxide, is an exception.

(*v*) Carbonates (with the exception of lithium) are soluble in water and stable towards heat.

(*vi*) They give acid salts but no basic salts.

(*vii*) They react with hydrogen on heating and under pressure to form solid 'salt-like' hydrides, M^+H^-.

SODIUM

2. **Historical.**—Sodium chloride (common salt), an important compound of sodium, has been known since very early times. Metallic sodium was isolated by the electrolysis of moist caustic soda (solid) by Sir Humphry Davy in 1807.

3. **Occurrence.**—Sodium occurs only in the combined state as :

(*i*) Sodium chloride, common salt found as rock salt, in sea water and in some inland lakes.

(*ii*) Sodium nitrate as Chile saltpetre or caliche in Chile (South America).

(*iii*) Sodium carbonate found as an efflorescent substance in the arid regions of many hot countries.

(*iv*) Borax, $Na_2B_4O_7.10H_2O$ is available in the crude form called *tincal* in California, Tibet and India (Ladakh and Kashmir).

4. **Manufacture.**—Sodium is prepared on a commercial scale by the electrolysis of fused caustic soda (*Castner's Process*) or fused sodium chloride (*Downs' Process*).

(i) **Castner's Process.** The type of cell used for the electrolysis of fused caustic soda is shown in Fig. 52·1. From the bottom of a cylindrical iron vessel rise the iron cathode kept in position by solid caustic soda. A cylindrical nickel anode surrounds the cathode near the top. A nickel wire-gauze cage separates the two and is provided with a receiver fitted with a loose cap at the top. A ring of gas burners below keeps the caustic soda in the fused state.

On passing electric current

resists oxidation).

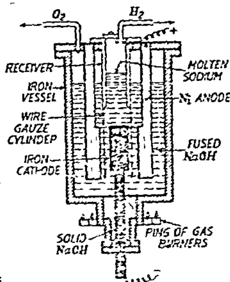
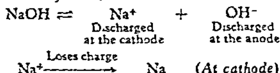


Fig. 52·1—Castner's Process for the manufacture of sodium.

Sodium being lighter rises up into the receiver and floats over fused sodium hydroxide. Wire gauze cylinder does not allow sodium globules to go astray and hydrogen evolved protects it from oxidation.

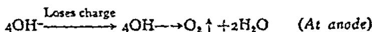
From the receiver it is removed from time to time with the help of perforated ladles which retain the liquid metal on account of its surface tension, but permit the molten sodium hydroxide to run through.

The various changes occurring during electrolysis may be represented ionically as follows :



$$NaOH \rightleftharpoons \underset{\text{Discharged at the cathode}}{Na^+} + \underset{\text{Discharged at the anode}}{OH^-}$$

$$Na^+ \xrightarrow{\text{Loses charge}} Na \quad (\textit{At cathode})$$



$$4OH^- \xrightarrow{\text{Loses charge}} 4OH \longrightarrow O_2\uparrow + 2H_2O \quad (\textit{At anode})$$

The oxygen escapes whereas water dissolves in molten caustic soda and is then electrolysed giving hydrogen (liberated at the cathode with sodium) and oxygen.

(*ii*) **Downs' Process.** In spite of the advantage of low temperature operation, Castner's Process is not extensively used today. Practically whole of the metal is now being manufactured by electrolysis of fused sodium chloride. Pure sodium chloride melts at 800°C but if potassium chloride and potassium fluoride be added to it, the melting point is lowered to 600°C.

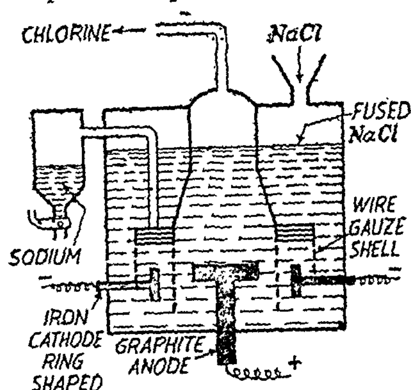


Fig. 2.52—Downs' Process.

Downs' electrolytic cell, used for the purpose, consists of an iron box through the bottom of which rises a circular carbon anode. The anode is surrounded by a ring shaped iron cathode enclosed in a wire-gauze shell which also acts as a partition and separates the two electrodes.

On electrolysis, chlorine is liberated at the anode and led out through an exit at the top. Sodium is liberated at the cathode and remains in the wire-gauze shell. Level of molten sodium rises and it overflows into a receiver. The chemical reaction involved in this process is as follows:



$$2NaCl \rightarrow 2Na + Cl_2$$

5. **Properties of Sodium.**

(*a*) **Physical.** (*i*) It is a silvery-white metal when freshly cut but is rapidly tarnished in air.

(*ii*) It is a soft metal which can be easily cut and is lighter than water (Sp. Gr.=0·972).

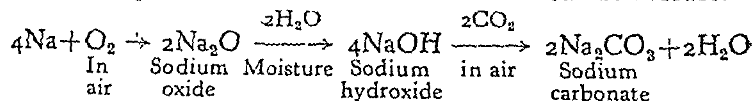
(*iii*) It is malleable and can be drawn into wires at ordinary temperature.

(*iv*) It is a good conductor of electricity.

(*v*) With mercury, it forms sodium amalgam.

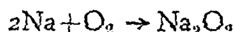
(*vi*) It melts at 97·5°C and boils at 880°C.

(*b*) **Chemical.** (*i*) *Action of air.* In moist air a layer of sodium oxide, hydroxide and carbonate is formed on the surface.



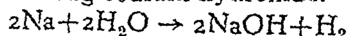
$$\underset{\text{In air}}{4Na + O_2} \rightarrow \underset{\text{Sodium oxide}}{2Na_2O} \xrightarrow[\text{Moisture}]{2H_2O} \underset{\text{Sodium hydroxide}}{4NaOH} \xrightarrow[\text{in air}]{2CO_2} \underset{\text{Sodium carbonate}}{2Na_2CO_3} + 2H_2O$$

When heated in air, it burns to form the peroxide.



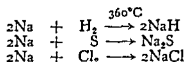
$$2Na + O_2 \rightarrow Na_2O_2$$

(*ii*) *Action of water.* It decomposes water vigorously liberating hydrogen and forming sodium hydroxide.



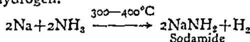
$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

(*iii*) *Combination with elements. It combines directly with* hydrogen, sulphur, halogens and other non-metals on heating.



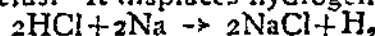
$$2Na + H_2 \xrightarrow{360°C} 2NaH$$
$$2Na + S \longrightarrow Na_2S$$
$$2Na + Cl_2 \longrightarrow 2NaCl$$

(iv) *Action of ammonia.* Sodium gives sodamide with ammonia liberating hydrogen.



$$2Na+2NH_3 \xrightarrow{300-400°C} \underset{\text{Sodamide}}{2NaNH_2}+H_2$$

(v) *Action of acids.* It displaces hydrogen from acids.



$$2HCl+2Na \rightarrow 2NaCl+H_2$$

(vi) *Reducing action.* Sodium acts as a reducing agent and reduces many oxides

6. Uses.—(i) For the preparation of sodium peroxide, sodamide and sodium cyanide.

(ii) Sodium amalgam is employed as a reducing agent.

(iii) As a reagent in organic chemistry.

COMPOUNDS OF SODIUM

7. *Sodium* **Peroxide,** *Na_2O_2.—It is prepared by heating* sodium in excess of air free from carbon dioxide. Sodium is cut into thin slices and placed in ammonium trays. With the help of a moving belt the trays are slowly moved through a heated tube (350°C) in a current of air, free from carbon dioxide (Fig. 52·3) blown from the opposite direction.

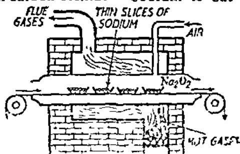
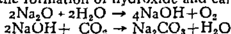


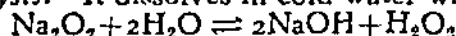
Fig 52·3—Manufacture of sodium peroxide.

Properties. (i) It is a pale yellow powder stable towards heat in dry air. It changes white in contact with moist air due to the formation of hydroxide and carbonate.



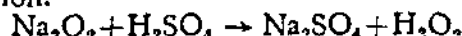
$$2Na_2O+2H_2O \rightarrow 4NaOH+O_2$$
$$2NaOH+ CO_2 \rightarrow Na_2CO_3+H_2O$$

(ii) *Hydrolysis.* It dissolves in cold water with hydrolysis.



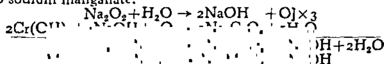
$$Na_2O_2+2H_2O \rightleftharpoons 2NaOH+H_2O_2$$

On heating hydrogen peroxide decomposes to give oxygen while on addition of ice-cold dilute acid the forward reaction proceeds to completion.



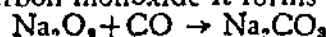
$$Na_2O_2+H_2SO_4 \rightarrow Na_2SO_4+H_2O_2$$

(iii) *Oxidising action.* Due to the ease with which it furnishes an atom of nascent oxygen, it acts as a powerful oxidising agent. It oxidises chromic hydroxide to sodium chromate and manganous salts to sodium manganate.



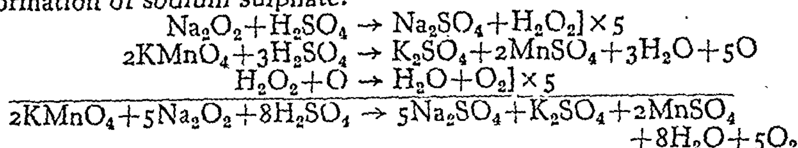
$$Na_2O_2+H_2O \rightarrow 2NaOH \quad +O] \times 3$$
$$2Cr(C \text{[illegible]} H_2O$$
[illegible] $)H+2H_2O$
[illegible] $)H$

(iv) With carbon monoxide it forms sodium carbonate.



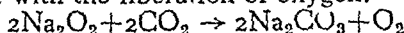
$$Na_2O_2+CO \rightarrow Na_2CO_3$$

(*v*) It reacts with acidified potassium permanganate with the formation of sodium sulphate.



$$Na_2O_2+H_2SO_4 \rightarrow Na_2SO_4+H_2O_2] \times 5$$
$$2KMnO_4+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+3H_2O+5O$$
$$H_2O_2+O \rightarrow H_2O+O_2] \times 5$$
$$2KMnO_4+5Na_2O_2+8H_2SO_4 \rightarrow 5Na_2SO_4+K_2SO_4+2MnSO_4+8H_2O+5O_2$$

Uses. (*i*) As an oxidising agent in the laboratory. (*ii*) As a source of oxygen under the name '*oxone*'. (*iii*) As a bleaching agent. (*iv*) For purifying air in submarines, etc., as it absorbs carbon dioxide with the liberation of oxygen.

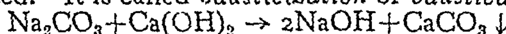


$$2Na_2O_2+2CO_2 \rightarrow 2Na_2CO_3+O_2$$

8. **Sodium Hydroxide, Caustic Soda, NaOH.**—Small quantities of pure sodium hydroxide needed in the laboratory may be prepared by the action of sodium on water.

Manufacture. Caustic soda is, however, prepared in industry by two methods given below :

(1) **Causticizing Process.** *Theory* : The process depends upon the fact that when milk of lime is added to sodium carbonate solution (*hot*), sodium hydroxide is obtained and calcium carbonate is precipitated. It is called *causticization* or *caustication.*



$$Na_2CO_3+Ca(OH)_2 \rightarrow 2NaOH+CaCO_3 \downarrow$$

Process. A dilute solution of sodium carbonate is run into big tanks and quicklime is placed in an iron cage dipping in the solution. The mass is agitated with the help of mechanical stirrers and blowing steam into the solution which is heated at the same time. This is continued until a test portion of the filtrate gives practically no effervescence with an acid. The precipitate ($CaCO_3$) is filtered off and the filtrate containing caustic soda is concentrated by evaporation in multiple effect vacuum evaporators and finally heated in cast-iron vessels over fire to get fused caustic soda.

(2) **Electrolytic Process.** For theory and manufacture of caustic soda using **Nelson cell** *a porous diaphragm cell* refer to page 2·71, while **Castner-Kellner cell,** *a mercury diaphragm cell* used for the manufacture of caustic soda, is given here.

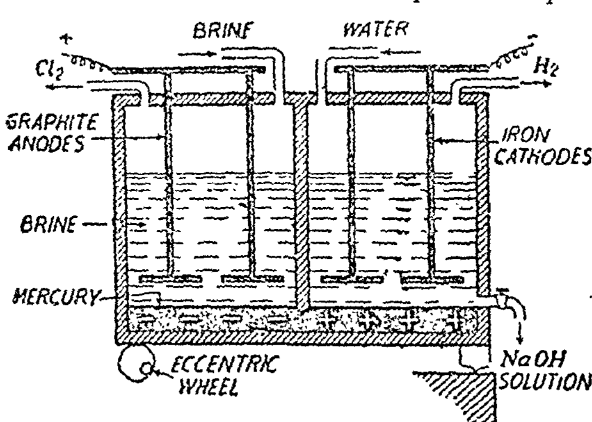


Fig. 52·4—Castner-Kellner cell for the manufacture of caustic soda.

It consists of a large rectangular trough with a layer of mercury at the bottom & divided into two compartments with a

slate partition not touching the bottom. Thus mercury in one compartment can flow into the other but any solution placed in one compartment cannot flow into the other. The left-hand compartment is fitted with graphite anodes dipping in brine whereas the right-hand compartment is fitted with iron cathodes dipping in any dilute caustic soda solution. Mercury acts as an intermediate electrode by induction, cathode on the left-hand side and anode on the right. The cell is kept rocking with the help of an eccentric wheel.

On passing electric current, chlorine is liberated at the anode in the left-hand compartment and is led out through an exit at the top. Sodium is liberated at the mercury cathode and forms amalgam with it. Sodium amalgam passes into the right-hand compartment due to the rocking motion and reacts with water there to give sodium hydroxide and hydrogen which escapes through the exit above. Caustic soda solution (concentrated) is removed periodically and water added.

The concentrated solution is evaporated to get fused caustic soda as given under causticizing process.

One of the best known mercury diaphragm cell is the Kellner-Solvay cell (Fig. 52·5), a modified form of the above. It uses graphite anodes and mercury cathode with no compartments. Mercury is entering on one side and sodium amalgam flowing out at the other into a vessel containing water where it decomposes to give caustic soda.

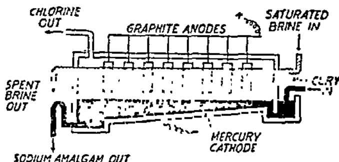


Fig. 52·5—Kellner-Solvay cell

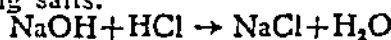
Estimate of Installed Capacity and Actual Production of Caustic Soda (in thousand tonnes) in India.

	1960-61	1965-66	1970-71	1975-76
Capacity	127	360	760	1,150
Production	92	300	600	1,000

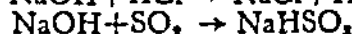
9. Properties of Sodium Hydroxide.

(*a*) Physical. It is a deliquescent white crystalline solid which readily absorbs moisture and carbon dioxide from the atmosphere. It is very soluble in water and heat is evolved during the dissolution. The solution is soapy to touch and is very corrosive. It melts easily at 318°C.

(*b*) Chemical. (*i*) *With acids*. It is a strong alkali and as such changes the colour of indicators and neutralizes all acids or acid oxides forming salts.

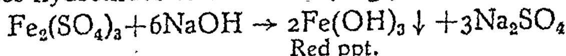


$$NaOH + HCl \rightarrow NaCl + H_2O$$



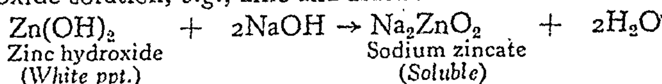
$$NaOH + SO_2 \rightarrow NaHSO_3$$

(*ii*) *Precipitation of hydroxides.* From metallic salt solutions it precipitates hydroxides of the metals, *e.g.*, with ferric sulphate.

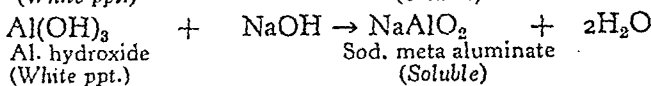


$$Fe_2(SO_4)_3 + 6NaOH \rightarrow \underset{\text{Red ppt.}}{2Fe(OH)_3\downarrow} + 3Na_2SO_4$$

In some cases the hydroxides dissolve in excess of sodium hydroxide solution, *e.g.*, zinc and aluminium.

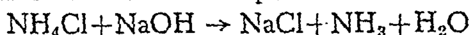


$$\underset{\substack{\text{Zinc hydroxide}\\(\textit{White ppt.})}}{Zn(OH)_2} + 2NaOH \rightarrow \underset{\substack{\text{Sodium zincate}\\(\textit{Soluble})}}{Na_2ZnO_2} + 2H_2O$$



$$\underset{\substack{\text{Al. hydroxide}\\(\textit{White ppt.})}}{Al(OH)_3} + NaOH \rightarrow \underset{\substack{\text{Sod. meta aluminate}\\(\textit{Soluble})}}{NaAlO_2} + 2H_2O$$

(*iii*) *With ammonium salts.* When heated with sodium hydroxide, ammonium salts decompose and liberate ammonia.



$$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$$

(*iv*) *With elements.* It reacts with a large number of elements, metals and non-metals. For example, its action on zinc, aluminium, tin and silicon (liberates hydrogen) ; chlorine, bromine and iodine ; sulphur (gives hypo) and phosphorus (gives phosphine) has already been discussed. Fused caustic soda attacks most of the metals.

10. **Uses of Sodium Hydroxide.**—(*i*) In the manufacture of soap, paper and viscose rayon (artificial silk).

(*ii*) In the manufacture of organic dyestuffs.

(*iii*) For the manufacture of sodium hypochlorite, chlorate and nitrite.

(*iv*) For petroleum industry for refining.

(*v*) For mercerizing cotton.

(*vi*) As a reagent in laboratory.

11. **Sodium Carbonate, Washing Soda, Na_2CO_3.**—Sodium carbonate has been known and used since very early times. Large deposits of crude sodium carbonate occur in certain areas, e.g., Wyoming (U.S.A.) and East Africa. These naturally-occurring deposits of sodium carbonate constitute valuable sources of supply.

In India, the important sodium carbonate manufacturing units are—M/s Tata Chemicals (Mithapur), M/s Dharangadhra Chemicals, The Saurashtra Chemicals and M/s Sahu Chemicals, Varanasi. The annual consumption of the material is estimated to be about 350,000 tonnes.

Estimate of Total Capacity and Production of Soda Ash (in thousand tonnes) in India.

	1960-61	1965-66	1970-71	1975-76
Capacity	270	360	720	1,100
Production	147	340	700	1,000

Manufacture. Three different methods employed for the manufacture of sodium carbonate are :

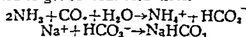
(1) **Ammonia Soda or Solvay Process.**

Theory. The process is based on the principle that when

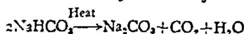
carbon dioxide is passed through brine previously saturated with ammonia, the various ions present in the solution are :

Na^+, Cl^-, HCO_3^- and NH_4^+.

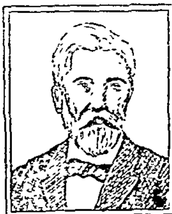
Out of various possible compounds, sodium bicarbonate being sparingly soluble in water, crystallizes out and is calcined to get sodium carbonate.



$$2NH_3+CO_2+H_2O \rightarrow NH_4^+ + HCO_3^-$$
$$Na^+ + HCO_3^- \rightarrow NaHCO_3$$



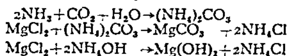
$$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3+CO_2+H_2O$$



Ernest Solvay
(1838 1922)
Belgian chemist ; is known

The Process. Different steps involved in the manufacture of sodium carbonate by this method are :

(*i*) **Saturation of Brine with Ammonia.** Ammonia gas mixed with a little carbon dioxide (from ammonia recovery tower ... in a *Saturatin*... magnesium or ... are precipitated as carbonates or hydroxides.



$$2NH_3+CO_2+H_2O \rightarrow (NH_4)_2CO_3$$
$$MgCl_2+(NH_4)_2CO_3 \rightarrow MgCO_3+2NH_4Cl$$
or
$$MgCl_2+2NH_4OH \rightarrow Mg(OH)_2+2NH_4Cl$$

The precipitate is removed by passing the solution through a *filter-press* and filtrate cooled in the *cooling pipe.*

(*ii*) **Carbonation.** Saturated brine is allowed to enter a little above the middle of the *carbonating tower* packed with perforated plates. It flows down slowly and meets an upward stream of carbon dioxide when tiny crystals of sodium bicarbonate appear (*see theory*).

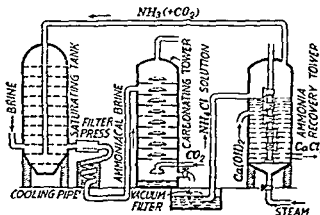
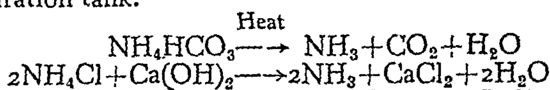


Fig. 52 6 – Ammonia soda or Solvay Process.

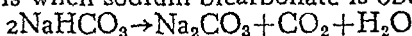
(*iii*) **Filtration.** The solution flowing out of the carbonating tower is filtered with the help of a vacuum filter. The solid sodium bicarbonate deposits on its surface and is scraped while the filtrate is pumped to the top of ammonia recovery tower.

(*iv*) **Ammonia Recovery.** The filtrate from the vacuum filter contains ammonium chloride and a little ammonium bicarbonate. It is made to flow down *ammonia recovery tower* while a current of steam is passing up and milk of lime is added at a point a little above the middle of the tower. Ammonium chloride and ammonium bicarbonate decompose as given below and ammonia recovered mixed with a little carbon dioxide is used for saturation of brine in the saturation tank.



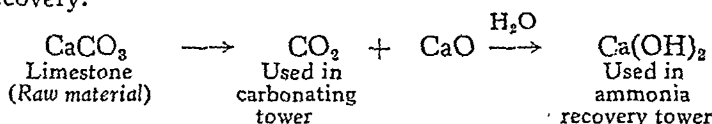
$$NH_4HCO_3 \xrightarrow{\text{Heat}} NH_3+CO_2+H_2O$$
$$2NH_4Cl+Ca(OH)_2 \longrightarrow 2NH_3+CaCl_2+2H_2O$$

(*v*) **Calcination of sodium bicarbonate.** Sodium bicarbonate obtained in (*iii*) above is heated strongly in specially designed cylindrical vessels when sodium bicarbonate is obtained.



$$2NaHCO_3 \rightarrow Na_2CO_3+CO_2+H_2O$$

Carbon dioxide required in carbonation is obtained by heating limestone. The residue is used as milk of lime for ammonia recovery.



$$\underset{\substack{\text{Limestone}\\(\textit{Raw material})}}{CaCO_3} \longrightarrow \underset{\substack{\text{Used in}\\\text{carbonating}\\\text{tower}}}{CO_2} + CaO \xrightarrow{H_2O} \underset{\substack{\text{Used in}\\\text{ammonia}\\\text{recovery tower}}}{Ca(OH)_2}$$

The only raw materials used are common salt, limestone and ammonia. The only by-product is calcium chloride for which new uses are being developed, *e.g.*, to keep down dust on highways and to make refrigeration brines. Thus the process is very cheap, self-contained and self-sufficient as indicated in Fig. 52·7 and the product obtained is of high purity. There are at present two plants working in India one at Mithapur and the other at Dharangadhra. The total capacity of the two plants is estimated to be about 54,000 tonnes.

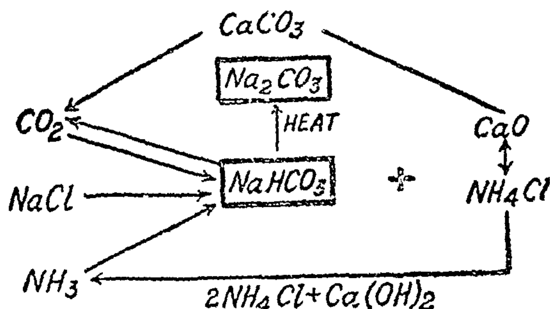


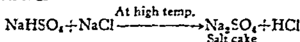
Fig. 52·7—Flow sheet for the Solvay Process.

(2) **Leblanc Process.** The manufacture of sodium carbonate by Leblanc Process involves the following steps :

(*i*) **The salt cake formation.** Common salt is heated strongly with sulphuric acid when salt cake, Na_2SO_4 is produced with the evolution of hydrochloric acid gas (*see* manufacture of hydrochloric acid, page 2·90).

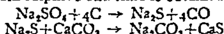


$$NaCl+H_2SO_4 \longrightarrow NaHSO_4+HCl$$



$$NaHSO_4 + NaCl \xrightarrow{\text{At high temp.}} \underset{\text{Salt cake}}{Na_2SO_4} + HCl$$

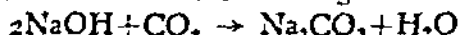
(ii) Black ash formation. Salt cake is pulverized and heated with limestone and coal dust in a cylindrical revolving furnace, when black ash containing about 45 per cent of sodium carbonate mixed with calcium sulphide and lime is obtained.



$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$
$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS$$

(iii) Extraction of sodium carbonate. Finely powdered black ash is treated with water in a number of iron tanks worked on the counter-current principle—fresh water comes in contact with exhausted black ash and concentrated solution treated with fresh black ash. The concentrated solution is evaporated to crystallization when we get crystals of *sodium carbonate*.

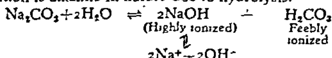
(3) Electrolytic Process. In the Nelson cell (page 2·71) used for the manufacture of caustic soda and chlorine, if carbon dioxide under pressure be blown along with steam, caustic soda produced will further react with carbon dioxide to give sodium carbonate.



$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

The solution is concentrated and crystallized. Wherever electricity is cheap, the method can be used with advantage.

12. **Properties of Sodium Carbonate.**—Sodium carbonate gives white crystals containing water of crystallization ($Na_2CO_3 \cdot 10H_2O$). The crystals effloresce on standing in air and crumble to powder, probably $Na_2CO_3 \cdot H_2O$. On heating it gives the anhydrous salt (m.p. 850°C) which is stable towards heat. It is soluble in water and the solution is alkaline in nature due to hydrolysis.



$$Na_2CO_3 + 2H_2O \rightleftharpoons \underset{\text{(Highly ionized)}}{2NaOH} + \underset{\text{Feebly ionized}}{H_2CO_3}$$
$$2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

It is readily decomposed by acids with effervescence due to the evolution of carbon dioxide.

13. **Uses of Sodium Carbonate.**—(i) In the manufacture of : (*a*) glass, (*b*) water glass, (*c*) caustic soda, (*d*) borax, and (*e*) soap powders.

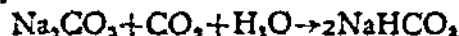
(*ii*) For softening water.

(*iii*) In laundry as washing soda.

(*iv*) As a laboratory reagent.

(*v*) As a starting material for the preparation of a number of other sodium compounds.

14. **Sodium Bicarbonate, Baking Soda, $NaHCO_3$.**—Commercial sodium bicarbonate is obtained as the primary product of the ammonia soda process. [illegible] bicarbonate by passing carbon [illegible] when bicarbonate is precip[illegible] and dried in air.



$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

It gives small white crystals sparingly soluble in water. The solution is alkaline in nature (gives yellow colour with methyl orange but no colour with phenolphthalein). It decomposes at 100°C with the evolution of carbon dioxide and leaving normal carbonate behind.



$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

It is used (*i*) in baking powders as leavening agent in cooking

(*ii*) In medicine to neutralize the acidity in the stomach.

(*iii*) In effervescent drinks, *e.g.*, Seidlitz powder.

15. **Sodium Chloride, Common Salt, NaCl.**—Common salt is found in sea water, in salt wells, inland lakes (*e.g.*, Sambhar in India and Lake Elton in Russia) and in deposits of rock salt in Himachal Pradesh (Mandi) and Khewra (Punjab, Pakistan).

Rock salt is dug out or dissolved in water if found very deep. The saturated solution is pumped out and evaporated to get the salt.

India is getting its supply of salt mainly from Sambhar lake and sea water. Sea water is run into lagoons with beds of clay to prevent percolation and allowed to evaporate. Clay deposits here and the saturated solution made to flow into other lagoons evaporates further when crude salt is deposited and is raked up.

In cold countries, like Russia, sea water is taken into pits where only water freezes at night leaving a concentrated solution. The percentage rises daily till it is 22 per cent and about 90 per cent of water has been removed. This is heated to get salt.

Purification. Sambhar salt contains 94% common salt and the rest is sodium carbonate and sodium sulphate. Common salt obtained from sea water contains 3·4% magnesium chloride, magnesium sulphate and calcium chloride. These impure samples of common salt are being purified in India as follows :

Impure salt is dissolved in water contained in big cement tanks. Some lime and alum is also added to these tanks. These help the suspended impurities to settle down. The clear solution is decanted into the iron pans and heated. As it gets concentrated, crystals of common salt separate and settle down. This is taken out, dried and bagged as "refined salt".

Sambhar salt can also be purified by fusion. Impure salt is mixed with a little washing soda heated to 800—850°C in a reverberatory furnace when it fuses. Sodium sulphate and sodium carbonate give a fusible slag with clay present in impure salt. This slag forms the lower layer in the furnace. The upper layer of the fused mass is allowed to flow into iron tanks and taken out on cooling. This is 98% pure and looks like a rock salt.

Properties. It is a colourless crystalline substance (cubic crystals, m.p. 820°C). Solubility does not vary appreciably with rise or fall of temperature. On heating the crystals break up with a crackling noise. Ordinary salt is slightly hygroscopic due to traces of magnesium and calcium chloride present. It gives the common reactions of a chloride and soluble sodium salt.

Uses. (*i*) It is an essential constituent of our diet.

(*ii*) As a preservative, *e.g.*, in packing and curing of meat and fish.

(*iii*) Mixed with ice, it gives a freezing mixture.

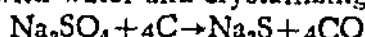
(*iv*) As a starting material for the manufacture of washing soda, caustic soda, chlorine, hydrochloric acid and many other sodium compounds.

(*v*) In the preparation of pottery glaze.

(*vi*) In the manufacture of soap for salting out.

16. **Sodium Sulphate, Glauber's Salt, Na_2SO_4.**—It is obtained as a by-product (salt cake) in the manufacture of hydrochloric acid. It is a colourless crystalline substance soluble in water. Its solubility curve (*see* page 1·193) shows a break at the point where decahydrate, $Na_2SO_4.10H_2O$ changes to the anhydrous salt. The crystals effloresce on standing in air. Sodium sulphate gives the usual reactions of sulphate. It is used in the manufacture of sodium sulphide, glass and as purgative.

17. **Sodium Sulphide, Na_2S.**—Sodium sulphide is formed when sodium hydrosulphide is treated with an equivalent amount ... tals of the ... it is pre- ... 1000°C extracting the mass with water and crystallizing.



$$Na_2SO_4+4C \rightarrow Na_2S+4CO$$

It is used in textile and paper industry, manufacture of dyes and to remove hair from hides.

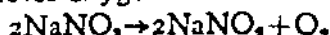
18. **Sodium Thiosulphate, Hypo, $Na_2S_2O_3$.**—*See* page 2·151.

19. ...

Sodium metabisulphite is used in photography while sodium bisulphite is used as an antichlor and as an antiseptic for preserving food.

20. **Sodium Nitrate, Chile Saltpetre, $NaNO_2$.**—Huge de- ...

It is a white deliquescent crystalline solid, very soluble in water. On heating it loses oxygen.

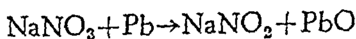


$$2NaNO_3 \rightarrow 2NaNO_2+O_2$$

It is used as a fertilizer in agriculture and for the manufacture of nitric acid, sodium nitrate and also potassium nitrate needed for the manufacture of gunpowder.

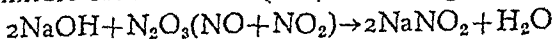
Sodium nitrate, being hygroscopic, cannot be used in gunpowder.

21. **Sodium Nitrate, $NaNO_2$.**—It is obtained by heating sodium nitrate or better by adding pieces of lead to fused sodium nitrate.



$$NaNO_3+Pb \rightarrow NaNO_2+PbO$$

It is now manufactured by passing into caustic soda an equimolecular mixture of nitric oxide (NO) and nitrogen dioxide (NO_2).

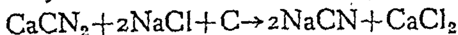


$$2NaOH+N_2O_3(NO+NO_2) \rightarrow 2NaNO_2+H_2O$$

It is a pale yellow, crystalline solid soluble in water. It gives the usual reactions of a nitrite (*see* page 2·192).

It is used in organic chemistry for diazotization.

22. **Sodium Cyanide, NaCN.**—Sodium cyanide is obtained when calcium cyanamide is heated with common salt and carbon.



$$CaCN_2+2NaCl+C \rightarrow 2NaCN+CaCl_2$$

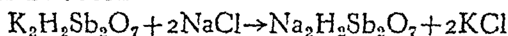
It is a very poisonous salt and is used in electroplating and in the metallurgy of gold and silver.

23. **Sodium Silicate, Water Glass, Na_2SiO_3.**—*See* page 2·263.

24. **Analytical Reactions of Sodium.**

(*i*) *Flame Test.* Sodium salts impart a persistent golden yellow colour to the flame.

(*ii*) *Confirmatory Test.* An aqueous solution of a sodium salt is made slightly alkaline with a few drops of caustic potash and treated with potassium hydrogen *pyroantimonate* when a white crystalline precipitate is obtained on scratching the sides of the test tube. This test is to be applied when all other basic radicals have been shown to be absent.



$$K_2H_2Sb_2O_7+2NaCl \rightarrow Na_2H_2Sb_2O_7+2KCl$$

(*iii*) *Magnesium Uranyl Acetate Test.** On adding this reagent to a sodium salt solution, yellow crystalline precipitate of sodium magnesium uranyl acetate, $NaMg(UO_2)_3.(CH_3COO)_2.9H_2O$ is obtained.

POTASSIUM

25. **Historical and Occurrence.**—Potassium carbonate has long been known as a constituent of wood-ashes. Metallic potassium was, however, isolated by Humphry Davy in 1808. The metal occurs only in the form of its compounds. For example—

(i) *Stassfurt deposits of Germany* are one of the principal sources of potassium compounds and contain carnallite, $KCl.MgCl_2.6H_2O$; sylvine, KCl ; and kainite, $K_2SO_4MgSO_4.MgCl_2 6H_2O$.

(ii) Workable deposits of potassium salts have been discovered in the U.S.A., Russia and Dead Sea.

(*iii*) *As Silicates.* Potassium aluminium silicates, *e.g.*, orthoclase, $K_2O.Al_2O_3 6SiO_2$ and mica, $KH_2Al_3(SiO_4)_3$ are common.

* This reagent is prepared by mixing 20 gm. of uranyl acetate with 66 gm. of magnesium acetate +25 c.c. glacial acetic acid and 175 c.c. water. The mixture is warmed, allowed to stand and filtered.

(*iv*) Nitre or Indian saltpetre, KNO_3 occurs as an efflorescence in arid regions of India (Punjab and West Bengal).

(*v*) Washings of sheep wool, residue left on carbonising beet sugar molasses are found to contain potassium salt.

26. **Preparation.**—Potassium is manufactured by electrolysis of fused potassium chloride alone or mixed with potassium fluoride as in the case of sodium. Electrolysis of fused caustic potash is unsatisfactory as the metal dissolves in the alkali.

27. **Properties.**—Potassium is a silvery-white metal (m.p. 62°C, b.p. 762°C). It is a light metal (Sp. Gr. 0·86) and can be cut with a knife. It resembles sodium in physical properties and is chemically more active.

COMPOUNDS OF POTASSIUM

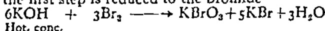
28. **Potassium Hydroxide, Caustic potash, KOH.**—Its methods of preparation and properties are similar to those given for caustic soda. It is a stronger alkali and is more soluble in alcohol. It is, therefore, used in organic chemistry in place of caustic soda. Being strongly deliquescent, it is used for drying gases, also for absorbing CO_2 and SO_2 in potash bulbs. It is used in the manufacture of soap.

29. **Potassium Chloride, KCl.**—It is found as sylvine, KCl and carnallite, $KCl.MgCl_2.6H_2O$ which is always found contaminated with magnesium sulphate and chloride.

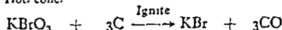
Potassium chloride is extracted from carnallite by boiling with the mother liquor from a previous operation, containing about 20 per cent magnesium chloride. Carnallite dissolves leaving other impurities undissolved. These are filtered off and the solution crystallized when potassium chloride (nearly 80 per cent) separates as cubic crystals leaving magnesium chloride in the mother liquor.

It is a white crystalline solid, fairly soluble in water. It is used as a fertilizer and for the preparation of other potassium compounds.

30. **Potassium Bromide, KBr.**—It is prepared: (*i*) By treating bromine with hot concentrated caustic potash, evaporating the solution and igniting the residue with carbon when the bromate obtained in the first step is reduced to the bromide



$$\underset{\text{Hot. conc.}}{6KOH} + 3Br_2 \longrightarrow KBrO_3 + 5KBr + 3H_2O$$



$$KBrO_3 + 3C \xrightarrow{\text{Ignite}} KBr + 3CO$$

(*ii*) By treating ferroso-ferric bromide, Fe_3Br_8 obtained as by-product during the manufacture of bromide, with potassium carbonate until neutral.



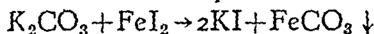
$$Fe_3Br_8 + 4K_2CO_3 + 4H_2O \rightarrow 2Fe(OH)_3 \downarrow + Fe(OH)_2 \downarrow + 8KBr + 4CO_2$$

Insoluble hydroxides are filtered off and potassium bromide in the solution crystallized.

It is a white crystalline solid, very soluble in water and gives the usual reactions of bromides.

Uses. It is used in medicine as a sedative to induce sleep. In photography it is used for the preparation of sensitive emulsion.

31. **Potassium Iodide, KI.**—Potassium iodide is prepared in the same way as bromide. Iron filings are treated with iodine under water to get iodide which is then treated with potassium carbonate. Method from caustic potash is also similar.



$$K_2CO_3 + FeI_2 \rightarrow 2KI + FeCO_3 \downarrow$$

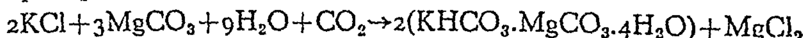
It is a white crystalline solid soluble in water and alcohol. It is used in medicine, photography, as a reagent in the laboratory and as a solvent for iodine.

32. **Potassium Chlorate $KClO_3$.**—*See* page 2·110.

33. **Potassium Carbonate, Potash or Pearl Ash, K_2CO_3.**—It was formerly obtained from wood-ashes by extracting with water and evaporating the solution or by calcining tartar. It is still obtained in this way from wool washings or residues left on igniting beet-root molasses.

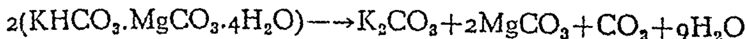
It can be prepared from potassium chloride by a modification of the Leblanc Process. *Solvay Process cannot be used for its manufacture as potassium bicarbonate is very soluble and does not crystallize like sodium bircarbonate.*

It is now being manufactured by the **Magnesia Process.** Carbon dioxide is passed into a solution of potassium chloride at 20°C in the presence of the hydrated magnesium carbonate when potassium hydrogen magnesium carbonate, $KHCO_3.MgCO_3.4H_2O$ is precipitated.



$$2KCl + 3MgCO_3 + 9H_2O + CO_2 \rightarrow 2(KHCO_3.MgCO_3.4H_2O) + MgCl_2$$

This is filtered and heated under pressure (140°C) when it gives potassium carbonate (soluble) and magnesium carbonate (insoluble) with the evolution of carbon dioxide.



$$2(KHCO_3.MgCO_3.4H_2O) \longrightarrow K_2CO_3 + 2MgCO_3 + CO_2 + 9H_2O$$

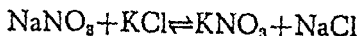
Potassium carbonate is extracted from the residue with water, concentrated and crystallized. Magnesium carbonate residue is used over again for fresh extraction.

It is a white crystalline, deliquescent substance fairly soluble in water. It resembles sodium carbonate in most of its reactions.

Uses. It finds use in the manufacture of soft soap, hard glass, caustic potash and other potassium compounds. It is also used in washing wool.

34. **Potassium Nitrate, Nitre or Indian Saltpetre, KNO_3** (शोरा).—Crude nitre occurs as an efflorescence on the surface of the earth in tropical countries, *e.g.*, in India. It is manufactured—

(*i*) *From Chile saltpetre.* A mixture of Chile saltpetre and potassium chloride in molecular proportions is dissolved in minimum quantity of boiling water.



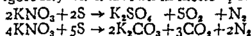
$$NaNO_3 + KCl \rightleftharpoons KNO_3 + NaCl$$

Out of these four salts, solubility of sodium chloride remains almost constant with rise of temperature (35·6 at 0°C and 39·8 at 100°C) whereas the solubility of potassium nitrate increases very rapidly (13·3 at 0°C and 246 at 100°C).

As the solution is kept boiling water evaporates and more of sodium chloride separates out. When enough of sodium chloride has been separated, the solution is cooled to crystallize out potassium nitrate.

(ii) *From crude Indian saltpetre.* The crude salt is dissolved in water and filtered. The filtrate, when concentrated and allowed to stand, deposits crystals of potassium nitrate. These may be further purified by crystallization.

It is a colourless, crystalline substance and differs from sodium nitrate in being deliquescent. It gives usual reactions of nitrates and is a good oxidising agent. Thus a piece of sulphur or charcoal burns vigorously when thrown in molten potassium nitrate.



$$2KNO_3+2S \rightarrow K_2SO_4+SO_2+N_2$$
$$4KNO_3+5S \rightarrow 2K_2CO_3+3CO_2+2N_2$$

Uses. (*i*) In the manufacture of gunpowder—an intimate mixture of nitre (6 parts), charcoal (1 part) and sulphur (1 part), and in fireworks.

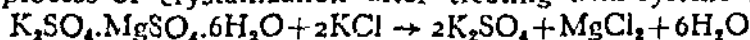
(ii) As an oxidising agent in the laboratory and industry, *e.g.*, in glass industry in the manufacture of flint glass.

(*iii*) For refrigeration.

(*iv*) In medicine.

35. **Potassium Nitrite, KNO_2.**—Its preparation and properties are similar to those given for sodium nitrite (*see* page 2·304). It forms white deliquescent crystals.

36. **Potassium Sulphate, K_2SO_4.**—It is manufactured from the naturally-occurring minerals, *e g*, Schonite, K_2SO_4 $MgSO_4$ $6H_2O$ by a process of crystallization after treating with Sylvine (KCl).



$$K_2SO_4.MgSO_4.6H_2O+2KCl \rightarrow 2K_2SO_4+MgCl_2+6H_2O$$

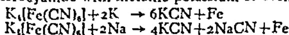
It forms colourless anhydrous crystals not very soluble in water (*cf.* $Na_2SO_4.10H_2O$) It is used as a fertilizer particularly for tobacco and wheat. It is also used for the manufacture of potash alum and in glass manufacture.

37. **Potassium Chromate and Potassium Dichromate** — *See under Chromium.*

38. **Potassium Ferrocyanide and Potassium Ferricyanide.**—*See under Iron.*

39. **Potassium Permanganate, $KMnO_4$.**—*See under Manganese.*

40. **Potassium Cyanide, KCN** —It is obtained by heating potassium ferrocyanide with metallic potassium or even sodium.



$$K_4[Fe(CN)_6]+2K \rightarrow 6KCN+Fe$$
$$K_4[Fe(CN)_6]+2Na \rightarrow 4KCN+2NaCN+Fe$$

The mixture of potassium and sodium cyanides obtained in the latter case is often sold as potassium cyanide.

It is a white crystalline powder, soluble in water and is a deadly poison. It is used in metallurgy, electroplating and as a laboratory reagent.

41. Analytical Tests for Potassium.

(*i*) *Flame Test.* Potassium salts impart a characteristic violet colour to the flame. This appears pink through blue glass.

(*ii*) *With Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$ solution* (freshly prepared), it gives a yellow precipitate of potassium cobaltinitrite, $K_3[Co(NO_2)_6]$.

(*iii*) *Tartaric acid Test.* With a concentrated solution of tartaric acid in the presence of alcohol, it gives a white crystalline precipitate of potassium hydrogen tartrate.

(*iv*) *Picric acid Test.* A solution of picric acid or sodium picrate gives a yellow precipitate of potassium picrate.

(*v*) *Hydrochloroplatinic acid,* H_2PtCl_6 forms with potassium salts a yellow precipitate of its potassium salt, K_2PtCl_6 in presence of alcohol.

AMMONIUM

42. Ammonium Radical or Alkali Metals.—The monovalent compound basic radical, NH_4^+ is called ammonium radical. It gives a series of well-defined compounds which closely resemble corresponding compounds of alkali metals. For example, NH_4OH is a base like NaOH or KOH. It is, therefore, discussed along with the alkali metals.

43. Ammonium Chloride, Sal ammoniac, NH_4Cl (*Nausadar*).—Fairly large amounts of crude ammonium chloride are available in Karnal district of Haryana. It is prepared by purifying the crude product by sublimation or by boiling ammonium sulphate solution with molecular proportion of sodium chloride.



$$(NH_4)_2SO_4 + 2NaCl \rightleftharpoons 2NH_4Cl + Na_2SO_4$$

Sodium sulphate being least soluble at high temperature, crystallizes out and is removed. The mother liquor on cooling gives crystals of ammonium chloride. This may be purified by sublimation.

It is a colourless or crystalline solid fairly soluble in water. On heating it dissociates as under:



$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

Uses. (*i*) In soldering and tinning. Acid obtained by its dissociation dissolves the metallic oxide layer and thus cleans the surface and enables the solder to "*bite*".

(*ii*) In Leclanche cells and dry cells.

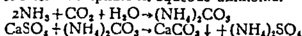
(*iii*) In dyeing, calico-printing and also in medicine.

(*iv*) As a reagent in laboratory.

44. **Ammonium Sulphate, $(NH_4)_2.SO_4$.**—It is manufactured from the ammoniacal liquor of gas works which contains about 17 gm. of ammonia in combination (*i.e.*, in the form of compounds) per litre. It is heated with lime by passing steam through it when ammonia is liberated. This is passed through 60% sulphuric acid contained in a lead lined tank, when ammonium sulphate crystals separate on cooling.

It is also manufactured by absorbing synthetic ammonia in sulphuric acid.

A new method consists in passing carbon dioxide gas through a suspension of calcium sulphate in aqueous ammonia.



$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$
$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + (NH_4)_2SO_4$$

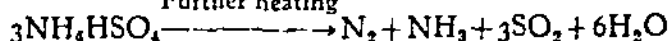
Calcium carbonate is filtered off and ammonium sulphate crystallized from the filtrate.

It is the principal fertilizer in India and is being manufactured mainly by two units—Sindri Fertilizer Factory and The Fertilizers and Chemicals, Travancore (FACT). The Sindri Fertilizer Factory is the largest of its kind in Asia.

It is the white crystalline solid which decomposes on heating as follows :



$$(NH_4)_2SO_4 \rightarrow NH_3 + NH_4HSO_4$$



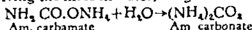
$$3NH_4HSO_4 \xrightarrow{\text{Further heating}} N_2 + NH_3 + 3SO_2 + 6H_2O$$

Uses. (*i*) As a fertilizer.

(*ii*) For the preparation of other ammonium salts.

45. **Ammonium Carbonate, $(NH_4)_2CO_3$**—Commercially available ammonium carbonate is manufactured by subliming a mixture of chalk and ammonium sulphate or chloride. The product is resublimed after adding a little water when we get a white semi-transparent fibrous mass with an outer layer of white opaque powder. The transparent mass is ammonium carbonate, $NH_2CO.ONH_4$ whereas the opaque powder is ammonium bicarbonate, NH_4HCO_3.

On dissolving the mass in water, we get ammonium carbonate.



$$\underset{\text{Am. carbamate}}{NH_2CO.ONH_4} + H_2O \rightarrow \underset{\text{Am carbonate}}{(NH_4)_2CO_3}$$

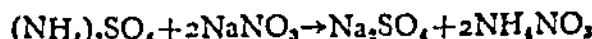
It is not very stable and on standing decomposes with the evolution of ammonia.



$$(NH_4)_2CO_3 \rightarrow NH_4HCO_3 + NH_3$$

It is used mainly as a smelling salt and as a reagent in the laboratory.

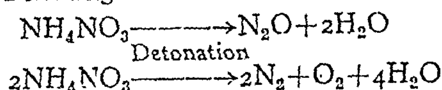
46. ***Ammonium Nitrate*, NH_4NO_3**—Ammonium nitrate is prepared by neutralizing concentrated nitric acid with ammonia gas or by double decomposition of ammonium sulphate and sodium nitrate.



$$(NH_4)_2SO_4 + 2NaNO_3 \rightarrow Na_2SO_4 + 2NH_4NO_3$$

$Na_2SO_4 \cdot 10H_2O$ crystallizes out first and from the mother liquor ammonium nitrate is recovered by evaporation.

It is a colourless crystalline substance readily soluble in water. It causes cooling on dissolution and is, therefore, used in freezing mixtures. On gentle heating it gives nitrous oxide but detonates on rapid heating.



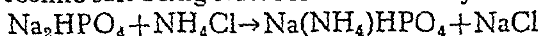
$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

$$2NH_4NO_3 \xrightarrow{\text{Detonation}} 2N_2 + O_2 + 4H_2O$$

It is used in making explosives, *Amatol* (salt+20% T.N.T.) and *Ammonal* (salt+Al-powder) and fertilizers.

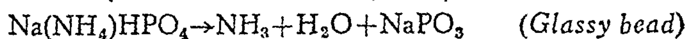
47. **Microcosmic Salt, $Na(NH_4).HPO_4.4H_2O$.**—It is prepared by dissolving molecular proportions of Na_2HPO_4 and NH_4Cl and crystallizing.

Microcosmic salt being least soluble of all crystallizes out first.

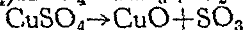


$$Na_2HPO_4 + NH_4Cl \rightarrow Na(NH_4)HPO_4 + NaCl$$

On heating it forms a transparent glassy bead of metaphosphate. This gives coloured beads of orthophosphates when heated with coloured salts (*microcosmic bead test*).



$$Na(NH_4)HPO_4 \rightarrow NH_3 + H_2O + NaPO_3 \qquad (\textit{Glassy bead})$$



$$CuSO_4 \rightarrow CuO + SO_3$$



$$CuO + NaPO_3 \rightarrow CuNaPO_4 \qquad (\textit{Blue bead})$$

It is used for detecting silica which being insoluble in $NaPO_3$ gives a cloudy bead.

48. **Analytical Tests for Ammonium.**—(*i*) On heating in a dry test tube ammonium salts give a white sublimate in the upper cooler parts of the test tube. Ammonia gas may also be evolved.

(*ii*) On heating with a concentrated caustic soda solution ammonium salts decompose with an evolution of ammonia.

(*iii*) The salt solution is made alkaline with caustic soda and then Nessler's reagent is added. A brown precipitate or a coloration is obtained.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Sodium+(*i*) Hydrogen, (*ii*) Sulphur, (*iii*) Chlorine, (*iv*) Ammonia, (*v*) Silica.
2. Sodium peroxide+(*i*) Water, (*ii*) Chromic hydroxide, (*iii*) Carbon monoxide, (*iv*) Carbon dioxide.
3. Sodium hydroxide+(*i*) HCl, SO_2 ; (*ii*) $Fe_2(SO_4)_3$, $ZnSO_4$, $Al_2(SO_4)_3$; (*iii*) Ammonium chloride.
4. Sodium chloride+Ammonia+Carbon dioxide.
5. Ferroso-ferric bromide+Potassium carbonate+water.
6. Passing carbon dioxide through potassium chloride in presence of hydrated magnesium carbonate.
7. Potassium hydrogen magnesium carbonate heated under pressure.
8. Burning of sulphur or charcoal in molten potassium nitrate.
9. Potassium ferrocyanide heated with potassium nitrate.
10. Ammonium carbonate+water.

QUESTIONS

Essay-type Questions

1. (a) Write what you know of the electrolytic method of extracting sodium.

(b) Indicate briefly how sodium carbonate can be converted into (i) sodium bicarbonate, and (ii) sodium hydroxide. *(Delhi H.S. 1963)*

2 Give a brief account of an electrolytic method for the manufacture of sodium hydroxide from sodium chloride.

Explain, with equations, the reactions of sodium hydroxide with (a) chlorine, (b) sulphur dioxide, (c) zinc, (d) zinc sulphate, (e) phosphorus. *(Delhi H S. 1965, 63 ; All India H.S. 1966 ; Punjab H S. 1963)*

3. How is caustic soda manufactured ? Indicate the important industrial uses of this compound.

(Delhi H S. 1967, 65, 63, 60 ; U.P. Board Inter. 1960 ; Kashmir 1960)

4 Explain, with equations, the reactions of NaOH with any of the following : (a) aluminium, (b) bromine, (c) phosphorus, (d) zinc sulphate, (e) sulphur, (f) carbon monoxide, (g) silver nitrate. *(M.P. Board Inter. 1964)*

5. Give a concise account of the various methods which are employed for the manufacture of sodium carbonate. What are the important uses of the compound ? *(Kashmir Inter. 1961)*

6. Describe Solvay's process for the manufacture of sodium carbonate. Can potassium carbonate be manufactured by this process ?
[illegible]

7. [illegible]

8. [illegible]
What are [illegible] manufactured by the Solvay process

9. Give the preparation, properties and uses of any three of the following :

(i) Potassium chloride (ii) Ammonium carbonate.
(iii) Potassium cyanide.
(iv) Sodium thiosulphate *(Delhi H.S 1972, 70, 68)*
(v) Potassium chlorate. *(Delhi H S. 1970, 68, 61, 60 ; Delhi Pre-Univ 1969 , Punjab 1960)*
(vi) Ammonium sulphate.
(vii) Salt ammoniac. *(Punjab Inter 1960)*
(viii) Sodium bicarbonate. *(Delhi H.S. 1963)*
(ix) Potassium iodide *(Delhi H.S. 1963)*
(x) Sodium hypochlorite *(Delhi H.S. 1965)*

10. Starting with potassium nitrate how would you obtain nitrogen, nitrous oxide, nitric oxide and nitrogen dioxide ? Give equations

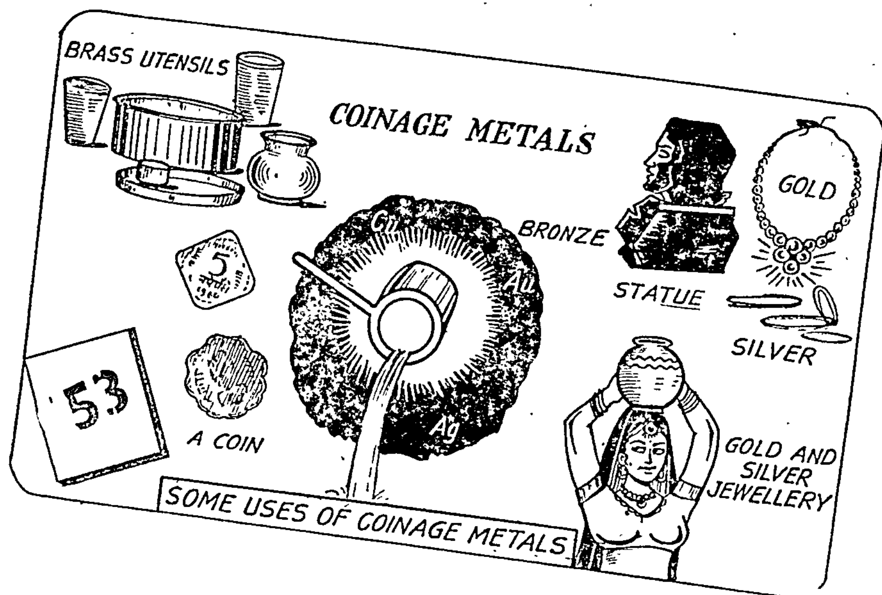
Test Your Understanding

11. Fill in the blanks in the following :

(i) Sodium is manufactured by electrolysis of fused or fused
(ii) Hydroxides of zinc and aluminium dissolve in caustic soda due to the formation of and respectively
(iii) From a solution containing Na^+, Cl^-, HCO_3^- and NH_4^+ ions, out of various compounds possible being sparingly soluble in water crystallises out first
(iv) Solvay process cannot be used for the manufacture of potassium carbonate as it is and does not like sodium bicarbonate.
(v) Ammonium sulphate is manufactured at Sindri by passing .... through a suspension of in aqueous

KEY

(i) Caustic soda, sodium chloride ; (ii) Sodium zincate, sodium meta-aluminate ; (iii) $NaHCO_3$; (iv) Very soluble, crystallise ; (v) Carbon dioxide gas, calcium sulphate, ammonia.



The Coinage Metals

1. **General.**—Copper, silver and gold are called the coinage metals. These constitute sub-group IB of the Periodic Table. Thus coinage metals have been grouped with alkali metals comprising sub-group IA, although there is no similarity between the members of two sub-groups except that all of them have one electron in their outermost orbit, *i.e.*, they are monovalent and their oxides are basic (slightly basic in case of coinage metals and strongly so in the case of the alkali metals).

Their inclusion in the same sub-group is justified by their similar behaviour and regular gradation in their properties from copper to gold as given below :

Resemblance among copper, silver and gold.

(*i*) *Occurrence.* All of them occur native and this is the reason why they have been known since pre-historic times.

(*ii*) *Physical Properties.* They are all hard, malleable and uctile metals with high melting points.

(*iii*) *Electronic Configuration.* They possess similar electronic onfiguration.

Copper (At. No. 29)=2, 8, 18, 1.
Silver (At. No. 47)=2, 8, 18, 18, 1.
Gold (At. No. 79)=2, 8, 18, 32, 18, 1.

(*iv*) *Reactivity.* They are weakly electropositive and unctive.

(*v*) *Variable Valency.* They show variable valency. For example : *cuprous*=1, *cupric*=2, *aurous*=1, *auric*=3.

(*vi*) *Displacement of the metals from their salts.* All the three metals can be displaced from the solution of their salts by zinc, iron or magnesium.

(*vii*) *Monovalent salts.* Their monovalent salts are colourless and generally insoluble in water. For example, CuCl and AgCl are both colourless and insoluble in water.

(*viii*) *Complex salts.* All of them form complex salts and in them metals may be a part of the complex cation or of the complex anion. For example :

$K_3Cu(CN)_4$ Pot. cuprocyanide	$KAg(CN)_2$ Pot. argentocyanide	$KAu(CN)_2$ Pot. aurocyanide

$Cu(NH_3)_4SO_4$ Cupri-ammine sulphate or Tetrammine- copper (II) sulphate	$Ag(NH_3)_2Cl$ Silver-ammine chloride or Diammine- silver (I) chloride

Gradation in their Properties. The three members show a regular gradation in their properties as we pass from copper to gold. For example :

(*i*) *Specific gravity and Specific heat.* The specific gravity of the metal increases while specific heat decreases regularly from copper to gold.

(*ii*) *Malleability and Ductility.* Malleability and ductility increases from copper to gold.

(*iii*) *Nobility.* They are all unreactive metals. The nobility increases from Cu → Ag → Au. For example, copper is acted upon by all mineral acids (dilute and concentrated), silver is dissolved by nitric acid (dilute and concentrated) and hot concentrated sulphuric acid. Gold is dissolved only by aqua regia.

(*iv*) *Number of salts.* Copper gives rise to a large number of salts, the number is small for silver while very few gold salts are known.

[illegible]

Silver and gold are not tarnished in air, the latter is not affected by oxygen at any temperature.

(*vi*) *Reduction of their salts.* Ferrous sulphate reduces gold salts readily into gold. Silver salts are reduced less readily whereas copper salts are not reduced at all.

The coinage metals, having practically nothing common [illegible] alkali metals, resemble nickel, platinum and palladium on one [illegible] and zinc, mercury and calcium on the other.

COPPER

2. **Historical.**—Copper was known to the earliest races of mankind. It was named as *cuprum* by the Romans because they used to get it from the island of Cyprus.

3. **Occurrence.**—Copper occurs native in the U.S.A., Mexico, Russia, China and Chile. Various natural ores of copper are :

(i) *Copper pyrites*, $CuFeS_2$; (ii) *Cuprite or ruby copper*, Cu_2O ; (iii) *Copper glance*, Cu_2S ; (iv) *Malachite*, $Cu(OH)_2CuCO_3$; and (v) *Azurite*, $Cu(OH)_2.2CuCO_3$.

Out of all these, copper pyrites is the principal ore of copper which yields nearly 75 per cent of the world production of copper.

Indian sources. Though there are numerous copper fields in India situated in Bihar, Orissa, Darjeeling, Kulu, Garhwal, Sikkim and Bhutan, extraction of copper is at present confined to only Mosabani area in the Singbhum district, Bihar, which is worked by The Indian Copper Corporation, established in 1924. This concern is the only producer of copper in India at present and is producing about 9,000 tons of copper annually which is only a small part of the country's requirements of this metal. The ore is crushed at the mine site and refined at their mills at Moubhandar where they possess a fully-equipped processing plant.

Recently, two important reserves of copper have been located at Khetri-Daribo area in Rajasthan and Rangpo area of Sikkim. The former is estimated at 28 million tonnes with an average copper content of 0·8% metal and the latter at about 0·35 million tonnes averaging about 6·24% of combined copper, lead and zinc. A project has been prepared for the establishment of a smelter with a capacity of 11,500 tonnes of electrolytic copper per annum at Khetri.

Estimates of Capacity and Production of Copper in India
(in thousand tonnes)

	1960-61	1965-66	1970-71	1975-76
Copper ingots				
Capacity	9	36	70	100
Production	9	36	70	100
Brass copper sheets and circles				
Capacity	*not available*	56	90	130
Production	51	56	90	130

4. **Extraction of Copper.**—The nature of the ore determines the method of treatment for extraction of the metal as given below :

(1) *From Oxide and Carbonate Ores.* The ore is crushed and then concentrated by Gravity Process (*see* page 2·287). The concentrated ore is calcined when it loses all volatile impurities and is converted into the oxide if not so already.

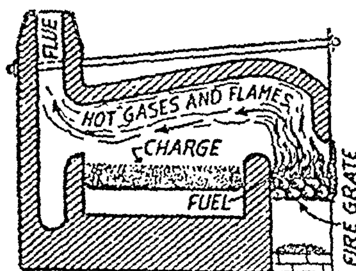
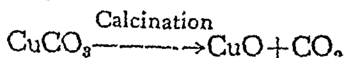


Fig. 53·1—Reverberatory Furnace.

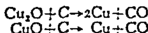


$$CuCO_3 \xrightarrow{\text{Calcination}} CuO + CO_2$$

Copper is extracted from the calcined ore.—

(*a*) **By smelting.** The calcined ore is smelted with carbon in the presence of a suitable flux

in reverberatory furnace. The oxide is reduced to metallic copper on smelting:



$$Cu_2O + C \rightarrow 2Cu + CO$$
$$CuO + C \rightarrow Cu + CO$$

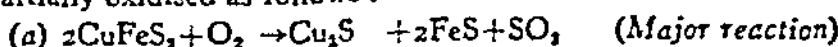
(*b*) **By the Leaching Process.** The concentrated oxide or carbonate is extracted with sulphuric acid. From the copper sulphate so obtained, metallic copper is precipitated with metallic iron or recovered by electrolysis.

(2) *From Sulphite Ores.* Copper pyrites constitute the principal sources of copper. The various steps involved in the process are :

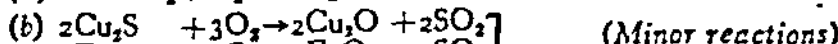
(*i*) **Crushing.** The ore is crushed in big jaw crushers and then finely powdered in ball mills and sieved.

(*ii*) **Concentration.** The finely powdered ore is concentrated by froth flotation process. (For details *see* page 2·287).

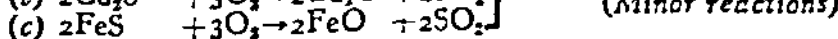
(*iii*) **Roasting.** The concentrated ore is heated strongly on the hearth of a reverberatory furnace (Fig. 53·1) in excess of air. Volatile impurities, *e.g.*, arsenic and antimony, are removed and the pyrites give a mixture of cuprous and ferrous sulphide, which are partially oxidised as follows :



(*a*) $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$ (*Major reaction*)



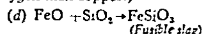
(*b*) $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$



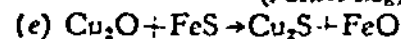
(*c*) $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$ (*Minor reactions*)

(*iv*) **Smelting.** The roasted ore is mixed with a little coke and sand and smelted in a water jacketed blast furnace about 15—20 feet high and 3—5 feet in diameter. It is a tower-like structure made of sheet steel and lined inside with fire-bricks (Fig. 53·2). A blast of air, necessary for combustion of coke and ore itself, is blown from below :

Reactions (*b*) and (*c*) started during roasting, proceed further and ferrous oxide formed combines with sand to form a fusible slag. Cuprous oxide formed reacts with ferrous sulphide to give ferrous oxide. (Iron has greater affinity for oxygen than copper.)



(*d*) $FeO + SiO_2 \rightarrow FeSiO_3$
(*Fusible slag*)



(*e*) $Cu_2O + FeS \rightarrow Cu_2S + FeO$

Slag is removed from the slag hole while a molten mass containing mostly cuprous sulphide with a little ferrous sulphide called matte is taken out from the exit below.

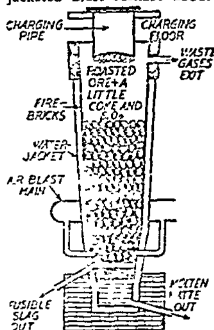


Fig. 53·2—Blast furnace for copper.

(*v*) **Bessemerization.** The molten matte is now transferred to a Bessemer converter—a pear-shaped furance (Fig. 53·3) made of steel plates and provided with a basic lining like that of lime or magnesium oxide. It is mounted on trunnions and can be tilted in any position. A blast of sand and air is blown through tuyeres in the side and a little above the bottom. Thus the molten metal drops below the level of tuyeres and escapes oxidation by the blast of air blown in.

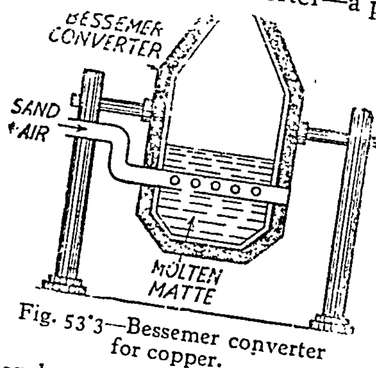
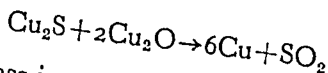


Fig. 53·3—Bessemer converter for copper.

Reactions (*b*)—(*e*) proceed to completion. When whole of iron has been slagged off, cuprous oxide reacts with cuprous sulphide to form copper.



(*f*) $$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

The molten mass is run into sand moulds and allowed to solidify when it gives out dissolved sulphur dioxide leaving blister type appearance on copper which is popularly known as **blister copper.**

(*vi*) **Purification of Blister copper.** Blister copper contains about 2 per cent of impurities consisting of iron, nickel, zinc, gold and silver and is refined as follows :

(*a*) **By Poling.** It is melted on the hearth of a reverberatory furnace in a stream of air and stirred with green wood poles. Any sulphur left is oxidised to sulphur dioxide and arsenic to As_4O_6 both of which escape as gases. The baser metal impurities are brought to the surface, exposed to the air blown in and oxidised. The oxides formed ither volatilise away or form lag while any copper oxide left n the metal is reduced to pper by the hydrocarbons ven out by the green poles.

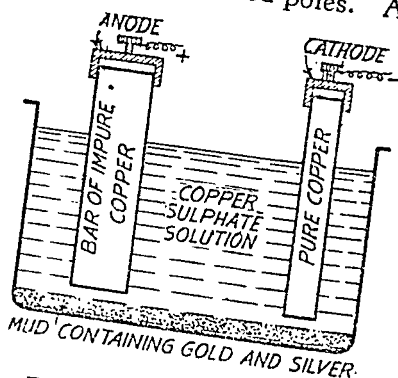


Fig. 53·4—Electrolytic refining of copper.

(*b*) **Electrolytic refining.** pure copper is made the ode in an electrolytic bath taining acidified copper sulte as electrolyte and the sheets of pure copper as cathode . 53·4). On passing electric current, pure copper is deposited

. . . . iron, nickel and zinc pass into anode mud as summarized in Fig. 53·5. The anode constantly dwindles while the cathode grows in size.

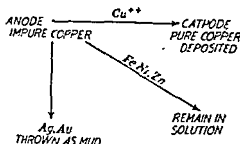


Fig. 53·5—Electrolytic refining of copper in outlines.

5. Properties of Copper.

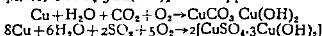
(*a*) *Physical.* (*i*) It is a heavy metal (Sp. Gr. = 8·94), reddish in colour. It melts at 1083°C and boils at 2320°C.

(*ii*) It is highly ductile, malleable and tenacious.

(*iii*) Next to silver it is the best conductor of heat and electricity. Traces of other metals greatly reduce the conductivity.

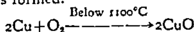
(*iv*) Molten copper has the property of occluding gases, *e.g.*, sulphur dioxide, hydrogen.

(*b*) *Chemical.* (*i*) Action of air. Dry air at ordinary temperature has no action on copper In moist air, it is superficially coated with a green basic carbonate called *verdigris*, $CuCO_3$, $Cu(OH)_2$ formed by the combined action of moisture, oxygen and carbon dioxide on copper. Sulphur dioxide in the air may also give basic sulphate, $CuSO_4 \cdot 3Cu(OH)_2$ with copper.

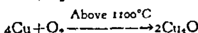


$$Cu + H_2O + CO_2 + O_2 \rightarrow CuCO_3\,Cu(OH)_2$$
$$8Cu + 6H_2O + 2SO_2 + 5O_2 \rightarrow 2[CuSO_4 \cdot 3Cu(OH)_2]$$

When heated in air, it gives cupric oxide but above 1100°C, cuprous oxide is formed.



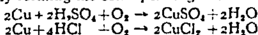
$$2Cu + O_2 \xrightarrow{\text{Below } 1100°C} 2CuO$$



$$4Cu + O_2 \xrightarrow{\text{Above } 1100°C} 2Cu_2O$$

(*ii*) Action of water. Water has no action on copper. Metal is attacked by steam only at white heat when slight oxidation occurs.

(*iii*) Action of acids. Dilute hydrochloric and sulphuric acids have no action on copper but in the presence of air, metal dissolves slowly forming the corresponding salt and water.



$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$
$$2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$$

In hot concentrated sulphuric acid, it dissolves with the evolution of sulphur dioxide (*see* page 2·131). With dilute nitric acid it gives nitric oxide whereas with concentrated nitric acid, it gives mainly nitrogen dioxide (*see* page 2·187).

(*iv*) Metal Displacement. Copper displaces silver, mercury and gold (less electropositive metals) from their salt solutions.

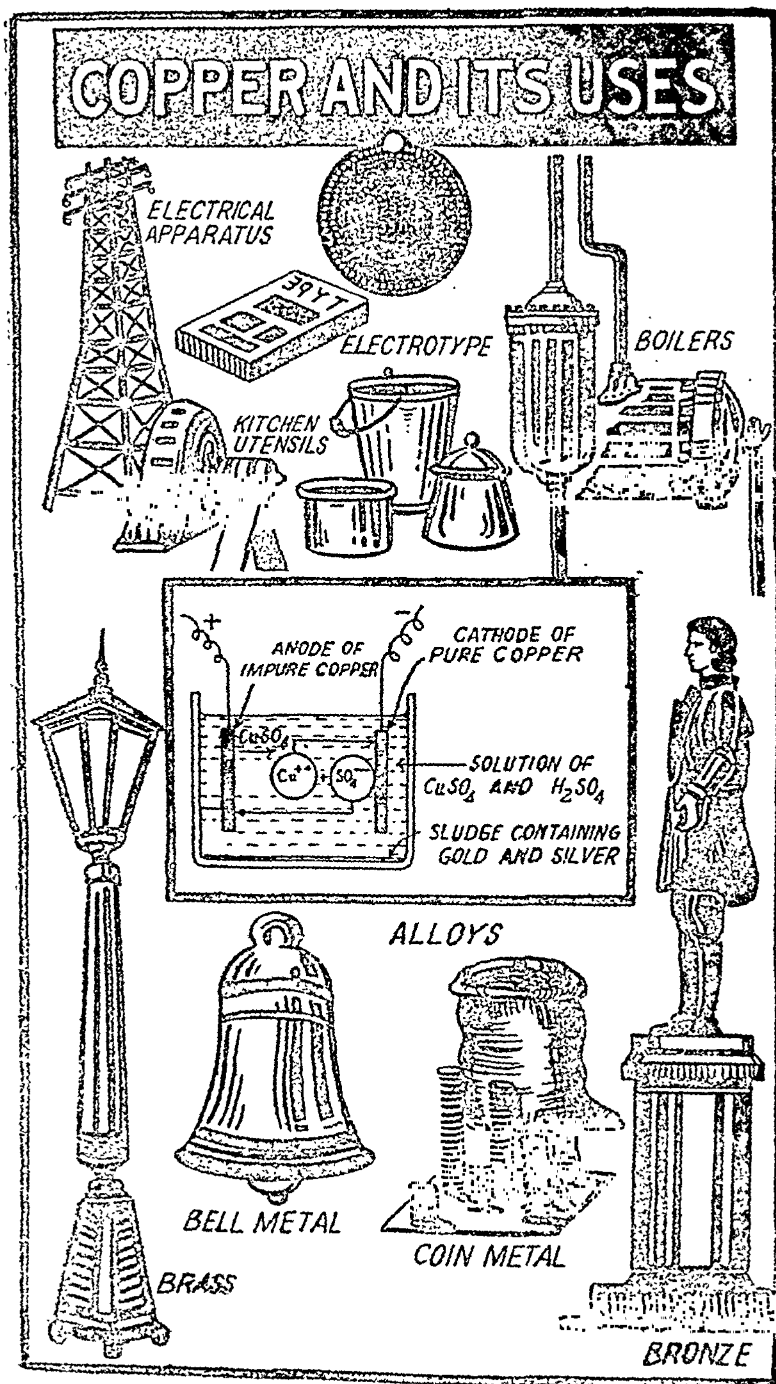
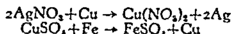

COPPER AND ITS USES
ELECTRICAL APPARATUS
TYPE
ELECTROTYPE
BOILERS
KITCHEN UTENSILS
ANODE OF IMPURE COPPER
CATHODE OF PURE COPPER
$CuSO_4$
Cu^{++}
SO_4^{--}
SOLUTION OF $CuSO_4$ AND H_2SO_4
SLUDGE CONTAINING GOLD AND SILVER
ALLOYS
BELL METAL
COIN METAL
BRASS
BRONZE

Fig. 53·6.

More electropositive metals (*e.g.*, Fe, Zn) displace copper from copper salt solutions.



$$2AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2Ag$$
$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

(*v*) **Action of Chlorine and Sulphur.** On heating with chlorine and sulphur, copper chloride ($CuCl_2$) and copper sulphide (CuS) are obtained.

6. **Uses of Copper.**—Stability of copper in air and water coupled with its excellent conductivity makes it a very useful metal for a number of purposes as given below :

(*i*) For making vacuum pans, heating utensils, calorimeters, and conductor coils.
(*ii*) For manufacturing electric goods, wires, etc.
(*iii*) In coinage.
(*iv*) For covering the bottoms of the wooden ships.
(*v*) In copper-plating, electrotyping, etc.
(*vi*) For manufacturing alloys.
(*vii*) In the preparation of copper salts largely used as insecticides.

7. **Alloys of Copper.**—Copper forms a number of alloys, the more important ones are given below .

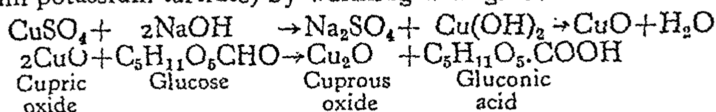
Name	Composition	Uses
1. Brass	Cu=60–90% Zn=10–40 %	Utensils, condenser tubes, sheets and cartridges
2. Bronze	Cu=88–96% Sn=4–12%	Utensils, statues and coins
3. Aluminium bronze	Cu=81·5–90% Al=7–12% Sn=0–0·5%	Golden yellow, non-corros[illegible] for cheap ornam[illegible] paint coinage and [illegible] exposed to corrod[illegible]
4. Bell metal	Cu=80% Sn=20%	Bells, gongs etc
5. Gun metal	Cu Sn Zn 88 10 2	Guns, gears [illegible]
6. German silver	Cu=25–50% Zn=25–35% Ni=15–35%	Utensils res[illegible]

COMPOUNDS OF COPPER

8. **Copper forms two Series** [illegible] variable valency and forms two se[illegible] it is monovalent whereas in cu[illegible]

these, the cupric salts are more stable. When cupric or cuprous is not stated in the case of a salt, cupric is implied, *e.g.*, copper sulphate implies cupric sulphate.

9. **Cuprous Oxide, Red Oxide of Copper, Cu_2O.**—It obtained by reduction of an alkaline solution of copper sulphate better still Fehling's solution ($CuSO_4$+NaOH+Rochelle sa sodium potassium tartrate) by warming with glucose.

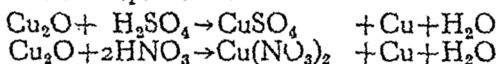


$$CuSO_4 + 2NaOH \rightarrow Na_2SO_4 + Cu(OH)_2 \rightarrow CuO + H_2O$$
$$\underset{\text{Cupric oxide}}{2CuO} + \underset{\text{Glucose}}{C_5H_{11}O_5CHO} \rightarrow \underset{\text{Cuprous oxide}}{Cu_2O} + \underset{\text{Gluconic acid}}{C_5H_{11}O_5.COOH}$$

It is yellow or red in colour depending upon its particle si It dissolves in ammonia in the absence of air and in the colourl solution thus obtained copper is present as a part of a comp $[Cu(NH_3)_2]OH$. It is stable towards heat above 1000°C but bel this temperature changes to cupric oxide, CuO. It is insoluble water and is readily reduced when heated in a current of hydro or coal gas.

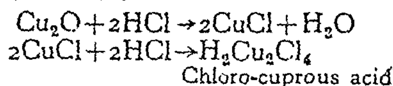
With acids it gives cuprous salts which are stable only if t form complex ions with the anions of the acids, *e.g.*, hydrochlo acid. In general, cupric salts are obtained with deposition copper which reacts further with the acid.

With nitric and sulphuric acids :



$$Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$$
$$Cu_2O + 2HNO_3 \rightarrow Cu(NO_3)_2 + Cu + H_2O$$

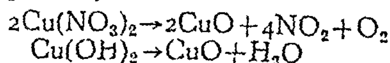
With hydrochloric acid :



$$Cu_2O + 2HCl \rightarrow 2CuCl + H_2O$$
$$2CuCl + 2HCl \rightarrow \underset{\text{Chloro-cuprous acid}}{H_2Cu_2Cl_4}$$

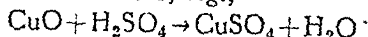
Uses. It is used as a colouring material in glass industry, pottery and in the manufacture of anti-rust paints.

10. **Cupric Oxide, Black Oxide of Copper, CuO.**—It prepared by igniting cupric nitrate (obtained by the action caustic soda on a copper salt).



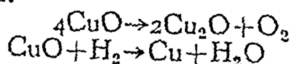
$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$$
$$Cu(OH)_2 \rightarrow CuO + H_2O$$

It is a black powder, insoluble in water. It is a typical b oxide and gives salts with acids, *e.g.*,



$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

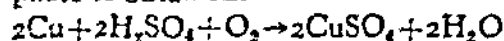
On strong heating (above 1000°C), it decomposes into c rous oxide and oxygen while heated oxide is reduced to coppe a current of hydrogen.



$$4CuO \rightarrow 2Cu_2O + O_2$$
$$CuO + H_2 \rightarrow Cu + H_2O$$

Uses. It finds use in organic analysis (*detection of ca and hydrogen*), in refining petroleum (*for removing sulphur*) an glass industry (*as colouring material*).

11. Cupric Sulphate, Blue Vitriol, $CuSO_4.5H_2O$ (नीला थोथा) It is prepared by spraying dilute sulphuric acid on copper scrap or turnings placed in a lead-lined tower while a current of air is passed up from below. The dilute solution is recirculated until a sufficient concentration of copper sulphate is obtained.



$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$

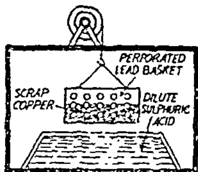
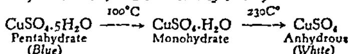


Fig. 53·7—Small scale manufacture of copper sulphate.

For small-scale manufacture, copper scrap is placed in a perforated lead basket which is alternately lowered and raised in a dilute sulphuric acid tank (Fig. 53·7). This is continued until a concentrated solution of copper sulphate is obtained which on standing deposits crystals of the copper pentahydrate, $CuSO_4.5H_2O$.

Properties. (*i*) It is a crystalline substance, blue in colour and soluble in water. The solution behaves acidic towards litmus due to hydrolysis.

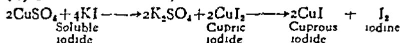
(*ii*) On heating, it loses its water of crystallization, finally giving a white powder which regains its blue colour when moistened with a drop of water (*used as a test of water*).



$$\underset{\text{(Blue)}}{\underset{\text{Pentahydrate}}{CuSO_4.5H_2O}} \xrightarrow{100°C} \underset{\text{Monohydrate}}{CuSO_4.H_2O} \xrightarrow{230°C} \underset{\text{(White)}}{\underset{\text{Anhydrous}}{CuSO_4}}$$

(*iii*) *With ammonium hydroxide*, the precipitate of cupric hydroxide first formed redissolves giving cuprammine sulphate $[Cu(NH_3)_4]SO_4$ (*complex compound*). This is Schweitzer's reagent used for dissolving cellulose in the manufacture of artificial silk.

(*iv*) *From soluble iodides*, it liberates iodine.



$$2CuSO_4 + \underset{\text{Soluble iodide}}{4KI} \longrightarrow 2K_2SO_4 + \underset{\text{Cupric iodide}}{2CuI_2} \longrightarrow \underset{\text{Cuprous iodide}}{2CuI} + \underset{\text{iodine}}{I_2}$$

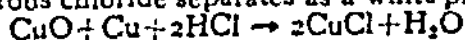
Uses. (*i*) As fungicide, *e.g.*, mixed with lime it gives *Bordeaux mixture* used for spraying vines, potatoes, etc.

(*ii*) In electroplating, electrotyping and electrorefining of copper.

(*iii*) In dyeing and calico printing.

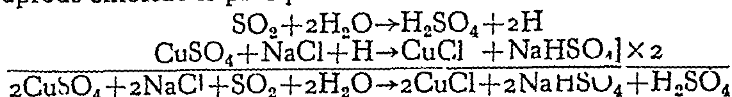
(*iv*) In medicine and in the laboratory for the preparation of other copper compounds, detecting water and in the preparation of absolute alcohol.

12. Cuprous Chloride, CuCl.—It is obtained by heating a mixture of cupric oxide and copper turnings with concentrated hydrochloric acid and pouring the solution in a large volume of water when cuprous chloride separates as a white precipitate.



$$CuO + Cu + 2HCl \rightarrow 2CuCl + H_2O$$

It is also prepared by passing sulphur dioxide through a solution of copper sulphate containing some sodium chloride when cuprous chloride is precipitated.



$$SO_2+2H_2O \rightarrow H_2SO_4+2H$$
$$[CuSO_4+NaCl+H \rightarrow CuCl+NaHSO_4] \times 2$$
$$\overline{2CuSO_4+2NaCl+SO_2+2H_2O \rightarrow 2CuCl+2NaHSO_4+H_2SO_4}$$

Properties. (*i*) It is a white solid almost insoluble in wat but soluble in concentrated hydrochloric acid with which it giv the complex acid, $HCuCl_2$.

(*ii*) It dissolves in ammonia forming the ammine, CuCl.NF

(*iii*) A solution of cuprous chloride in hydrochloric acid ammonia is used in gas analysis for the absorption of carb monoxide with which it forms the colourless crystals of carbon compound, $CuCl.CO.2H_2O$.

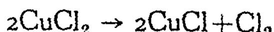
(*iv*) In air, it is slowly oxidised to a green basic cup chloride, $3CuO.CuCl_2.3H_2O$.

(*v*) An ammoniacal solution of cuprous chloride reacts wi acetylene to give red precipitate of cuprous acetylide, $Cu_2C_2.H_2C$

Uses. In the gas analysis for absorbing carbon monoxi and acetylene.

13. **Cupric Chloride,** $CuCl_2.2H_2O$.—It is obtained by d solving cupric oxide or carbonate in hydrochloric acid and concer rating the solution when cupric chloride crystallizes out. The a hydrous salt cannot be prepared by heating the hydrated crystals it gets hydrolysed. It is, therefore, obtained by burning copper a current of chlorine.

Properties. Hydrated crystals are greenish in colour wher as the anhydrous salt is a brown powder. It is soluble in wat and decomposes on heating with the liberation of chlorine.



$$2CuCl_2 \rightarrow 2CuCl+Cl_2$$

Uses. (*i*) As catalyst in the Deacon's process.

(*ii*) In making pigments.

14. **Cupric Nitrate,** $Cu(NO_3)_2$.—It is conveniently pr pared by dissolving cupric oxide or carbonate in nitric acid. T solution is concentrated when deep blue crystals of cupric nitra $Cu(NO_3)_2.3H_2O$ are obtained.

The anhydrous salt (*white*) can be prepared by treating h drated crystals with nitrogen pentoxide in nitric acid.

It decomposes on heating as given below and is an oxidisi agent.

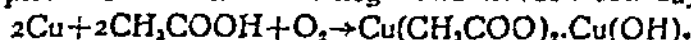


$$2Cu(NO_3)_2 \rightarrow 2CuO+4NO_2+O_2$$

15. **Cupric Sulphide, CuS.**—It is obtained as a bla precipitate when hydrogen sulphide is passed into a solution of cupric salt, *e.g.*, (copper sulphate) acidified with hydrochloric aci It dissolves in hot dilute nitric acid and in potassium cyanide wi which it gives a complex compound, $K_2[Cu(CN)_4]$.

16. Copper Acetates.—*The normal acetate*, $Cu(CH_3COO)_2.H_2O$ is prepared by dissolving cupric oxide or verdigris in acetic acid. It is used in the manufacture of pigments

Basic copper acetate (verdigris) is obtained by exposing copper plates to the action of vinegar and air for a few days.



$$2Cu+2CH_3COOH+O_2 \rightarrow Cu(CH_3COO)_2.Cu(OH)_2$$

It is used in paint manufacture, dyeing and calico-printing.

17. Analytical Tests for Copper.

(*a*) Dry Tests. (*i*) *Colour.* Copper salts are generally bluish-green or blue in colour.

(*ii*) *Charcoal cavity test.* When heated in a charcoal cavity in a reducing flame, copper salts leave reddish scales.

(*iii*) *Flame test.* A paste of copper salt in concentrated hydrochloric acid, imparts a bluish-green colour to flame.

(*iv*) *Borax bead test.* Copper salts give a borax bead which is blue in the oxidising flame and red in the reducing flame (due to the formation of cuprous oxide).

(*b*) Wet Tests. (*i*) *With hydrogen sulphide*, an acidified copper salt solution gives a black precipitate of copper sulphide insoluble in yellow ammonium sulphide but soluble in dilute nitric acid.

(*ii*) *With ammonium hydroxide*, a bluish-green precipitate first formed redissolves giving deep blue solution of a complex *cupriammine salt* (*see* page 2·323).

(*iii*) *With caustic soda*, a bluish precipitate of cupric hydroxide is obtained. This changes black on heating due to the formation of cupric oxide, CuO.

(*iv*) A piece of iron or zinc when placed in copper salts solution precipitates copper.

(*v*) *With potassium ferrocyanide*, copper salts give a chocolate precipitate of copper ferrocyanide.

SILVER

18. Historical.—Silver has been known since ancient times and was probably used as money.

19. Occurrence.—In the *combined state*, silver occurs as—

(*i*) *Argentite or silver glance*, Ag_2S which occurs as such or associated with galena (lead ore) and copper ore as impurity.

(*ii*) *Pyrargyrite* or ruby silver ore—Ag_3SbS_3.

(*iii*) *Horn silver* or chlorargyrite—AgCl.

Large quantities of silver occur *native* in Mexico, the U.S.A., Canada and Peru. Silver is recovered from the *anode mud* (obtained during electrolytic refining of copper) and from argentiferous lead obtained from argentiferous galena (lead sulphide containing argentite as impurity).

(ii) *Silver is more soluble in molten zinc than in molten lead.*

(iii) *Zinc-silver alloy solidifies earlier than molten lead.*

(iv) *Zinc being volatile can be separated from silver by distillation.*

Argentiferous lead is melted and treated with molten zinc which forms the upper layer. Most of silver, being more soluble in zinc, passes into the upper zinc layer. On cooling the zinc-silver alloy (*upper layer*) solidifies and is removed with perforated [illegible] fresh molten zinc and [illegible] repeated a number of [illegible] distilled, when zinc distils over and silver contaminated with a little lead is left behind.

Purification. Lead present as impurity in the silver obtained above is purified by *cupellation*. Impure silver is heated in a bone-ash crucible used as a removable hearth of a reverberatory furnace (Fig. 53·8) in a blast of air. Lead present is oxidised to litharge (PbO) and blown away till pure silver flashes out, *i.e.*, shining surface of silver is visible. This may be further purified by the electrolytic process.

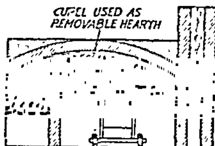


Fig. 53·8—Purification of silver by cupellation

(*b*) **Pattinson's Process.** Desilverization of lead containing very small amounts of silver is carried out by *Pattinson's Process*. This is based on the fact that on cooling a molten lead-silver alloy, lead separates until concentration of silver rises to 2·4 per cent in the alloy and the entire mass solidifies *en bloc*.

Argentiferous lead is melted and cooled. Crystals of lead, very much poorer in silver, separate and are removed with perforated ladles. The process of melting and cooling is repeated as above till the entire mass solidifies *en bloc*. Silver is recovered *from the alloy by cupellation.*

22. **Electrolytic Method for Extraction of Silver.**—In this method argentiferous lead is refined electrolytically using fluosilicic acid (H_2SiF_6) and lead fluosilicate ($PbSiF_6$) mixture containing some gelatine as electrolyte. Thin sheets of pure lead [illegible] into anodes. [illegible] is anode mud [illegible] ils.

Anodic mud obtained during the electrolytic refining of copper (*see* page 2·318) can similarly by worked for the extraction of silver.

23. Properties of Silver.

(*a*) **Physical.** (*i*) Silver is a white heavy metal with a brilliant lustre (Sp. Gr.=10·5).

(*ii*) It is hard, very malleable and ductile.

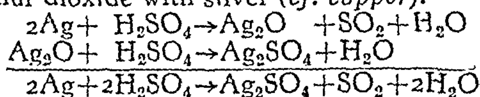
(*iii*) It is the best conductor of heat and electricity.

(*iv*) When melted, it absorbs oxygen which it again expels on cooling. Globules of molten silver are thrown off. This is called "*spitting*" of silver and can be prevented by covering the molten metal with a layer of charcoal.

(*b*) **Chemical.** (*i*) It is monovalent, electropositive.

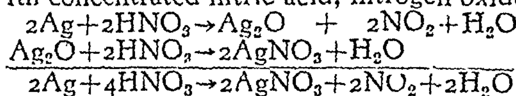
(*ii*) *Action of air and water.* Silver undergoes no change in contact with water or pure air.

(*iii*) *Action of alkalis and acids.* Silver is unaffected by caustic alkalis and vegetable acids. Dilute hydrochloric and sulphuric acids also have no action. Hot concentrated sulphuric acid gives sulphur dioxide with silver (*cf. copper*).



$$2Ag + H_2SO_4 \rightarrow Ag_2O + SO_2 + H_2O$$
$$Ag_2O + H_2SO_4 \rightarrow Ag_2SO_4 + H_2O$$
$$\overline{2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O}$$

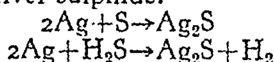
In dilute nitric acid, it readily dissolves liberating nitric oxide. With concentrated nitric acid, nitrogen oxide is evolved.



$$2Ag + 2HNO_3 \rightarrow Ag_2O + 2NO_2 + H_2O$$
$$Ag_2O + 2HNO_3 \rightarrow 2AgNO_3 + H_2O$$
$$\overline{2Ag + 4HNO_3 \rightarrow 2AgNO_3 + 2NO_2 + 2H_2O}$$

or $$Ag + 2HNO_3 \rightarrow AgNO_3 + NO_2 + H_2O$$

(*iv*) *Action of sulphur.* Silver reacts with sulphur compounds to form black silver sulphide.



$$2Ag + S \rightarrow Ag_2S$$
$$2Ag + H_2S \rightarrow Ag_2S + H_2$$

Foods rich in sulphur, e.g., mustard and egg yolk, tarnish silverware black.

(*v*) *Action of halogens.* Silver directly combines with halogens to form silver halides.

24. Uses of Silver.—(*i*) For coinage, jewellery and decorative purposes. It is alloyed with copper for making coins.

(*ii*) In silver plating metallic articles, *e.g.*, tableware (*see* page 1·206).

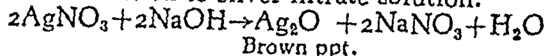
(*iii*) Most modern mirrors are plated with silver.

(*iv*) In preparation of silver salts used in silvering of mirrors photography and medicine. Silver amalgam is used in filling teeth

(*v*) Pure silver is beaten into thin leaves and used in medicines as a tonic.

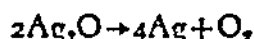
COMPOUNDS OF SILVER

25. Silver oxide, Ag_2O.—It is precipitated by adding sodium hydroxide solution to silver nitrate solution.



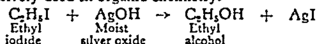
$$2AgNO_3 + 2NaOH \rightarrow \underset{\text{Brown ppt.}}{Ag_2O} + 2NaNO_3 + H_2O$$

The brown precipitate of silver oxide is soluble in ammonium hydroxide due to the formation of complex *silver-ammine* hydroxide $[Ag(NH_3)_2]OH$ (*cf.* cupri-ammine salts). On heating it decomposes and gives out oxygen.



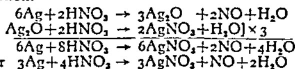
$$2Ag_2O \rightarrow 4Ag + O_2$$

Moist silver oxide behaves like silver hydroxide, AgOH and is extensively used in organic chemistry.



$$\underset{\text{Ethyl iodide}}{C_2H_5I} + \underset{\text{Moist silver oxide}}{AgOH} \rightarrow \underset{\text{Ethyl alcohol}}{C_2H_5OH} + AgI$$

26. **Silver Nitrate, Lunar Caustic, $AgNO_3$.**—Silver nitrate is prepared by dissolving the metal in dilute nitric acid and crystallizing the solution.



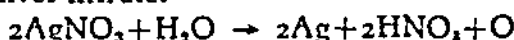
$$6Ag + 2HNO_3 \rightarrow 3Ag_2O + 2NO + H_2O$$
$$Ag_2O + 2HNO_3 \rightarrow 2AgNO_3 + H_2O] \times 3$$
$$6Ag + 8HNO_3 \rightarrow 6AgNO_3 + 2NO + 4H_2O$$
$$\text{or } 3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$$

Silver nitrate forms large rhombic plates very soluble in water. On heating it gives metallic silver and nitrogen dioxide.



$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

It gives a black stain when it comes in contact with skin or cloth due to its reduction to metallic silver. (*Finely divided silver is black in colour.*) Its use as a caustic is based on this oxidising property of silver nitrate.



$$2AgNO_3 + H_2O \rightarrow 2Ag + 2HNO_3 + O$$

Silver nitrate as an analytical reagent. Silver nitrate precipitates silver from salt solutions Colour of the precipitate together with the information whether it is soluble in nitric acid and ammonium hydroxide or not, gives us a clue regarding identity of the acid radical as given below :

Colour of the precipitate	Solubility in		Inference
	Nitric acid	Ammonia	
White	Insoluble	Soluble	Chloride, Cyanide
White	Soluble	,,	Oxalate, Borate
Straw yellow	Insoluble	Sparingly ,,	Bromide
Yellow	,,	Insoluble	Iodide
Yellow	Soluble	Soluble	Phosphate, Arsenite
Red	,,	,,	Chromate, Arsenate
Changes colour White→Black	,,	,,	Thiosulphate
Black	,,	,,	Sulphide

Uses of Silver nitrite. (*i*) In marking inks and hair dyes.

(*ii*) In medicines in dilute solution as caustic for granular lids and unwanted skin growths.

(*iii*) For preparing silver halides used in photography.

(*iv*) In silvering mirrors.

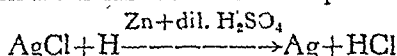
(*v*) As a reagent in the laboratory.

27. **Preparation of Silver nitrates from Silver containing Copper.**—Pure silver nitrate can be prepared from silver containing copper as an impurity, *e.g.*, a silver coin made of silver alloyed with 10 per cent copper.

Impure silver is dissolved in nitric acid when both silver and copper form their nitrates. From the solution obtained, silver chloride is precipitated with dilute hydrochloric acid. The precipitate is filtered, washed with hot water and dried. Silver chloride is next reduced to silver by any of the following three methods :

(*i*) Moist silver chloride is boiled with sodium hydroxide solution and glucose when silver chloride is first changed to silver oxide which is next reduced to silver.

(*ii*) Moist silver chloride is reduced to metallic silver with nascent hydrogen from zinc and dilute sulphuric acid.



$$AgCl + H \xrightarrow{Zn + dil.\ H_2SO_4} Ag + HCl$$

(iii) Dry silver chloride is fused with sodium carbonate in a crucible when a silver bead is obtained.

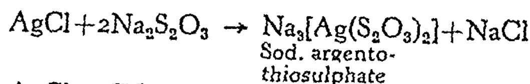


$$4AgCl + 2Na_2CO_3 \rightarrow 4Ag + 2CO_2 + O_2 + 4NaCl$$

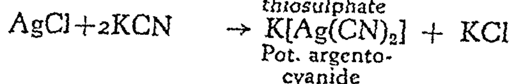
Pure silver so obtained is dissolved in dilute nitric acid to give silver nitrate. This is concentrated and crystallized.

Thus silver can be recovered from a silver coin or silver halides obtained as precipitates in the laboratory.

28. **Silver Halides.**—Chloride, bromide and iodide of silver are obtained as curdy precipitates by adding silver nitrate to the corresponding halide solutions. These are all insoluble in nitric acid. White precipitate of silver chloride is soluble in ammonium hydroxide due to the formation of soluble complex, silver-ammine chloride, $Ag(NH_3)_2Cl$. Straw yellow precipitate of silver bromide is sparingly soluble in ammonium hydroxide whereas yellow precipitate of silver iodide is insoluble. They are all affected by light and are soluble in sodium thiosulphate as well as a soluble cyanide with which they give argento-thiosulphates, and argento-cyanides.



$$AgCl + 2Na_2S_2O_3 \rightarrow \underset{\text{Sod. argento-thiosulphate}}{Na_3[Ag(S_2O_3)_2]} + NaCl$$



$$AgCl + 2KCN \rightarrow \underset{\text{Pot. argento-cyanide}}{K[Ag(CN)_2]} + KCl$$

Silver fluoride is soluble in water and is not precipitated by adding silver nitrate to a soluble fluoride. This is prepared by

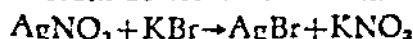
dissolving silver oxide or carbonate in hydrofluoric acid. It is a deliquescent substance.

PHOTOGRAPHY

29. **Historical.**—Sixteenth century alchemists noticed that silver halides darkened when exposed to light. This was later used in preparation of photographs. The first photograph was produced by Wedgwood in 1800 whereas a permanent photograph was made only by Daguerre in 1839.

30. **Photographic Process.**—Modern photography involves six major steps as given below :

(i) **Preparation of sensitive plates or films.** Sensitive emulsion is a paste of colloidal silver bromide or silver iodide in gelatin It is obtained by adding ammoniacal silver nitrate solution to ammonium bromide solution containing gelatin.

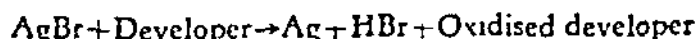


$$AgNO_3+KBr \rightarrow AgBr+KNO_3$$

This is allowed to stand in a warm room (about 54°C) for some time when silver bromide particles grow in size and at the same time become more sensitive to light. The process is called *ripening*. After sufficient time has been allowed, the interval depending upon the desired sensitiveness, the emulsion is applied to glass plates or celluloid films in dust-free dark rooms. The glass plates or celluloid films serve merely to hold the sensitive emulsion.

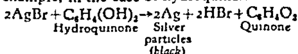
(ii) **Exposure.** The sensitive plate or film is mounted in a camera and exposed for a few seconds to the image of a properly focussed object. Actual time of exposure depends upon the relative sensitiveness of the plate, intensity of light and size of the aperture. Different parts of the body reflect different quantities of light and affect the plate proportionally. Under the effect of light decomposition of silver bromide takes place in traces, where it is illuminated forming extremely minute particles or nuclei of silver. There is no visible effect but in the affected parts the emulsion becomes more easily reducible to the formation of silver nuclei while the image remains latent.

(iii) **Developing.** A developer is a weak reducing agent, *e.g.*, ferrous oxalate, or an alkaline solution of quinol, metol or [illegible] follows :



$$AgBr+\text{Developer} \rightarrow Ag+HBr+\text{Oxidised developer}$$

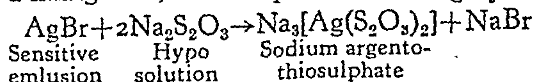
For example, in the case of hydroquinone



$$\underset{\text{Hydroquinone}}{2AgBr+C_6H_4(OH)_2} \rightarrow \underset{\substack{\text{Silver}\\\text{particles}\\(black)}}{2Ag}+2HBr+\underset{\text{Quinone}}{C_6H_4O_2}$$

The image becomes visible but its shade is in negative relationship with the shade of the object. The plate is, therefore, called the *negative plate*.

(*iv*) **Fixing.** The sensitive emulsion still present on the negative plate at white centres is dissolved out in hypo solution ($Na_2S_2O_3$) in a fixing bath, and the plate is thoroughly washed.



$$\underset{\text{Sensitive emulsion}}{AgBr} + \underset{\text{Hypo solution}}{2Na_2S_2O_3} \rightarrow \underset{\text{Sodium argento-thiosulphate}}{Na_3[Ag(S_2O_3)_2]} + NaBr$$

Now the negative plate which was all along kept in dark or faint red light can be taken into light.

(*v*) **Printing.** The processes used in the preparation of negative are again repeated in the process of printing. Two types of printing papers used are :

(*a*) *P.O.P. (printing out paper) coated with silver chloride and silver citrate mixture.* It is placed under the negative and exposed to light in a printing frame. The process being slow can be watched and controlled. When the image of required shade is obtained, it is fixed and toned.

(*b*) *"Velox" brand bromide paper.* It is more sensitive and needs short exposure followed by developing, fixing and toning.

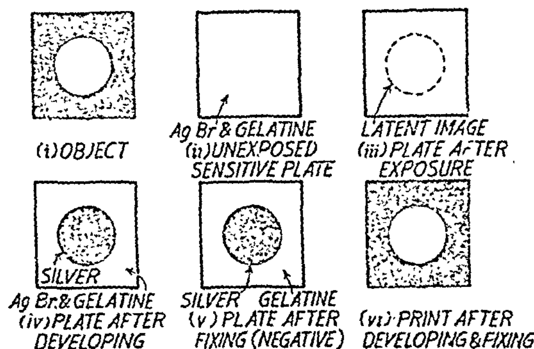
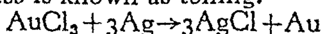


Fig. 53·9—Different steps involved in photography.

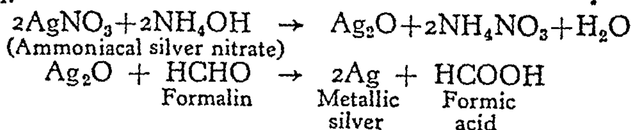
Different steps given above are summarized in the diagram (Fig. 53·9).

(*vi*) **Toning.** The black shade of the photograph can be changed to a beautiful purple or fine steel grey by dipping in gold chloride and potassium chloroplatinate (K_2PtCl_6) solution respectively. The process is known as toning.



$$AuCl_3 + 3Ag \rightarrow 3AgCl + Au$$

31. **Silvering of Mirrors.**—*The art of depositing a thin uniform layer of silver on a clean glass surface is called silvering.* The process is based on the reduction of an ammoniacal solution of silver nitrate by some reducing agent like tartrates, glucose or formalin.



$$\underset{\text{(Ammoniacal silver nitrate)}}{2AgNO_3 + 2NH_4OH} \rightarrow Ag_2O + 2NH_4NO_3 + H_2O$$

$$Ag_2O + \underset{\text{Formalin}}{HCHO} \rightarrow \underset{\text{Metallic silver}}{2Ag} + \underset{\text{Formic acid}}{HCOOH}$$

Two separate solutions are prepared :

Solution I. By dissolving 20 gm. of silver nitrate in 150 c.c. water and adding ammonia until the precipitate first formed redissolves. More water is added and the solution made to 320 c.c.

Solution II. It consists of a solution of a reducing agent.

The glass plate to be silvered is cleaned thoroughly and fixed in a dish with wax so that only one side of it is exposed. The two solutions obtained above are mixed in a proper proportion and poured over the fixed glass plate which is given a slow to and fro motion Reduction occurs and a fine, thin layer of silver is deposited on the glass plate. It is washed, dried and polished by rubbing gently with soft cotton wool. It is then given a thin protective coating of red lead and turpentine mixture.

Reflecting surfaces, plane and curved mirrors, are all obtained like this.

32. **Tests for Silver.** (i) *Charcoal cavity test.* On heating a silver salt with fusion mixture in a charcoal cavity, it gives a malleable bead with an incrustation of the oxide.

(ii) *Hydrochloric acid test.* On adding a few drops of hydrochloric acid an aqueous solution of a silver salt gives a white precipitate of silver chloride insoluble in nitric acid but soluble in ammonium hydroxide.

(iii) *Chromate test.* On adding potassium chromate to the neutral solution of soluble silver salt, a brick red precipitate of silver chromate is obtained, which is soluble both in nitric acid and ammonia.



$$2AgNO_3 + K_2CrO_4 \rightarrow \underset{\text{Brick red ppt.}}{Ag_2CrO_4 \downarrow} + 2KNO_3$$

(iv) *Silver mirror test.* To a silver salt solution is added ammonia until the precipitate first formed redissolves. The ammoniacal solution is heated with sodium tartrate when a shining silver mirror is formed on the inner side of the test tube.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Copper pyrites + Oxygen (roasting).
2. Cuprous sulphide + Oxygen („).
3. Ferrous sulphide + Oxygen („).
4. Ferrous oxide + silica.
5. Cuprous oxide + Ferrous sulphide.
6. Cuprous sulphide + Cuprous oxide.
7. Copper + (i) Oxygen (heated below and above 1100°C), (ii) Dil. sulphuric and hydrochloric acid in presence of air, (iii) Hot conc. sulphuric acid ; (iv) Nitric acid, (v) Ferric sulphate.
8. Alkaline copper sulphate + Glucose
9. Copper sulphate + (i) Potassium iodide, (ii) Sodium chloride + Sulphur dioxide.
10. Cupric oxide + Copper + Hydrochloric acid
11. Action of heat on (i) Copper nitrate, (ii) Cupric chloride, (iii) Silver oxide.
12. Sodium sulphide + Sodium cyanide
13. Sodium argentocyanide + Zinc
14. Silver + (i) Hot conc. sulphuric acid ; (ii) Nitric acid ; (iii) Sulphur ; (iv) Hydrogen sulphide.
15. Silver nitrate + Caustic soda solution.

16. Silver chloride+(*i*) Zinc and dil. sulphuric acid ; (*ii*) fused with sodium carbonate ; (*iii*) Sodium thiosulphate ; (*iv*) Ammonia.

17. Hydroquinone+Silver bromide.

18. Ammoniacal silver nitrate+Formalin.

QUESTIONS

Essay-type Questions

1. Justify the inclusion of copper, silver and gold in the same family. (*Bombay Inter. 1963 Supp.*)

2. Give the name and composition of the common ore of copper. Describe the steps involved in the metallurgy of copper. Give the preparation and uses of the chlorides and sulphates of the metal. (*Punjab H.S. 1963 ; Pre-Univ. 1964, 62, Inter. 1969 ; U.P. Board Inter. 1963 ; Delhi H.S. 1971, 67*)

3. Name the copper ore available in India. Describe in detail the extraction of copper in pure state from copper pyrites. Give equations to represent the action of nitric, hydrochloric and sulphuric acids on copper. What is "German silver" ? (*Punjab Inter. 1960*)

4. Write a short account of the process employed in the extraction of silver from its ores. How would you prepare silver nitrate from silver chloride ?

Explain giving equations, the chemistry of photography. (*Kashmir Inter. 1962 ; Delhi H.S. 1968, 64, 62 ; Delhi Pre-Medical 1963*)

5. Name the chief ores of silver. Give one method used at present for the extraction of silver. What are the important properties and uses of the metal ? (*Delhi H.S. 1964*)

6. Write short notes on :

(*a*) Photography. (*All India H.S. 1968 ; Delhi H.S. 1966 ; Punjab H.S. 1963 ; Punjab Pre-Univ. 1963*)

(*b*) Silvering of glass. (*c*) Cupellation.

(*d*) Desilverization of lead. (*e*) Silvering and silver plating.

(*f*) Conversion of silver nitrate into silver. (*Delhi H.S. 1968*)

7. Give the preparation, properties and uses of :

(*i*) Copper sulphate. (*Punjab H.S. 1963 ; Punjab Pre-Univ. 1963*)

(*ii*) Cuprous chloride.

(*iii*) Silver nitrate. (*Delhi H S. 1965, 61 ; Punjab Inter. 1960*)

8. Give the composition of Bronze, German silver and Duralumin. (*All India H.S. 1968*)

Test Your Understanding

9. Fill in the blanks in the following :

(*i*) Principal ores of copper and silver are......and......respectively.

(*ii*) German silver contains no silver. It is an alloy of......, ...and......

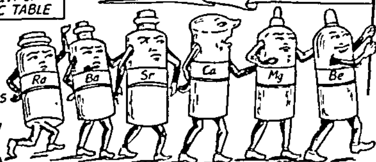
(*iii*) Copper sulphate liberates......from soluble iodides.

(*iv*) Developer is a weak......

(*v*) The fixing bath contains......solution which dissolves......still present on the negative plate.

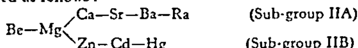
KEY

(*i*) Copper pyrites, Argentite or silver glance ; (*ii*) Copper, zinc, nickel ; (*iii*) Iodine ; (*iv*) Reducing agent ; (*v*) Hypo, sensitive emulsion.



Alkaline Earth Metals

1. General.—The elements beryllium, magnesium, calcium, strontium, barium, and radium constitute Group IIA of the Periodic Table. The metals calcium, ... monly known as the alkaline earth m ... zinc, cadmium and mercury whic ... Periodic Table. Although beryllium and magnesium are included in Group IIA, they are closely related to elements of Group IIB also. The mutual relationship between the sub-groups can be represented as follows:



2. Group Characteristics.—(i) All of them have similar electronic configuration as given below There are two electrons in the outermost energy level of their atoms and they are all divalent, strongly electropositive next to alkali metals

Element	Atomic number	Number of electrons in each energy level						
		K	L	M	N	O	P	Q
Beryllium	4	2	2					
Magnesium	12	2	8	2				
Calcium	20	2	8	8	2			
Strontium	38	2	8	18	8	2		
Barium	56	2	8	18	18	8	2	
Radium	88	2	8	18	32	18	8	2

(*ii*) They are all silvery-white metals which are light, tough and malleable.

(*iii*) They are all very active chemically and oxidise or burn readily in air. The activity increases with the atomic weight.

(*iv*) They react with water forming hydroxides and liberating hydrogen.

(*v*) *They combine directly with the halogens and nitrogen forming halides and nitrides respectively.*

(*vi*) Their hydroxides increase in solubility and basic properties whereas sulphates decrease in solubility with the rise of atomic weight.

(*vii*) Their carbonates decompose when heated.

It is difficult to classify beryllium and magnesium. They resemble calcium, strontium and barium in some respects and in other respects they show similarities with zinc and cadmium. For example :

(*i*) They are not oxidised in dry air.

(*ii*) They do not react with water in the cold like calcium and others. Beryllium does not decompose it even when it is hot.

(*iii*) Their salts do not impart any colour to the flame like those of calcium, strontium and barium which impart brick-red, crimson and apple green colour respectively.

(*iv*) Their sulphates are more soluble.

MAGNESIUM

3. **Occurrence.**—Magnesium occurs in nature in the combined state, not free, as *Magnesite*, $MgCO_3$; *Dolomite*, $MgCO_3.CaCO_3$; *Epsom salt*, $MgSO_4.7H_2O$; *Carnallite*, $MgCl_2.KCl.6H_2O$ and also in talc, asbestos and spinal.

4. **Preparation.**—Magnesium is prepared by the electrolysis of fused anhydrous magnesium chloride in an atmosphere of coal gas. Some sodium or potassium chloride is also added to the fused electrolyte to lower the melting point and to increase the conductivity. The cast iron or steel vessel serves as the cathode while a graphite rod is used as the anode. The anode is surrounded by a porcelain hood through which the liberated chlorine escapes. Molten magnesium being lighter than the electrolyte rises to the surface in the outer compartment and is removed at intervals with a ladle.

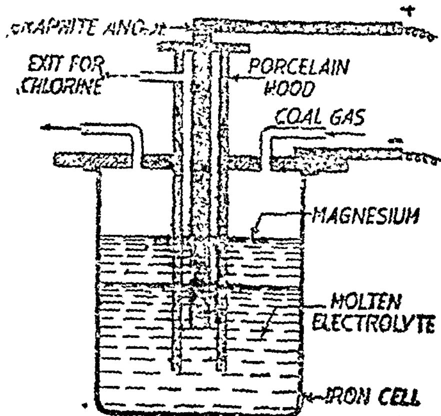
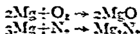


Fig. 54·1—Preparation of magnesium by electrolytic method.

5. Properties of Magnesium.—(i) It is [illegible] silvery-white and [illegible] C. It is a light [illegible]

(ii) It is divalent, electropositive. It atomic weight is 24 and atomic number, 12.

(iii) *Burning.* It burns in air with a dazzling white light, rich in ultra-violet rays, forming magnesium oxide and magnesium nitride.



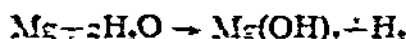
$$2Mg + O_2 \rightarrow 2MgO$$
$$3Mg + N_2 \rightarrow Mg_3N_2$$

It is an active metal and continues burning even in an atmosphere of steam and carbon dioxide.



$$2Mg + CO_2 \rightarrow 2MgO + C$$

(iv) *Action of water.* It decomposes water slowly when it is cold due to the formation of a protective magnesium hydroxide layer. With boiling water or steam the decomposition is quite rapid.



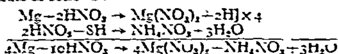
$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

(v) *Action of acids.* Dilute hydrochloric or sulphuric acid gives hydrogen with magnesium.



$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

With dilute nitric acid, part of the hydrogen liberated is oxidised by nitric acid which itself is reduced to a variety of products depending upon the concentration. For example, it gives ammonium nitrate as follows :



$$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + 2H] \times 4$$
$$2HNO_3 + 8H \rightarrow NH_4NO_3 + 3H_2O$$
$$4Mg + 10HNO_3 \rightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$$

6. Uses of Magnesium.—(i) In flashlight photography, signal flares, pyrotechnics and in fireworks.

(ii) As a reducing agent and a de-oxidiser in metallurgy and as a fuse in aluminothermic process.

(iii) In the manufacture of its alloys which have uses of their own as given below :

Magnalium (Al 85 to 99% ; Mg 1 to 15%) is hard, tough and light. It can be easily worked on the lathe and is used for making balance beams and light instruments.

Electron (Mg 95% ; Zn 5%) is used in the construction of aircraft.

COMPOUNDS OF MAGNESIUM

7. Magnesium Oxide, Magnesia, MgO.—It is prepared by gently heating the natural carbonate.

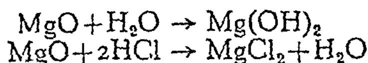


$$MgCO_3 \rightarrow MgO + CO_2$$

(*i*) It is a white powder, very resistant to change at high temperatures. As such it is used as refractory material for lining electric furnaces.

(*ii*) When moistened with a saturated solution of magnesium chloride, it sets to a firm hard cement (*Sorel's cement*) used as a stopping for teeth.

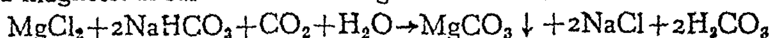
(*iii*) *Basic nature.* With water it forms the hydroxide and with acids it forms salts.



$$MgO + H_2O \rightarrow Mg(OH)_2$$
$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

Uses. (*i*) As a refractory lining in electric furnaces. (*ii*) As a basic lining in smelting process of metallurgy. (*iii*) Mixed with asbestos it is used as an insulator for lagging steam pipes and boilers. (*iv*) The flocculent form of the oxide is used as a rubber filler. (*v*) In medicine.

8. **Magnesium Carbonate, $MgCO_3$.**—It is the normal carbonate which occurs in nature as the mineral *magnesite*. It is precipitated by the addition of sodium carbonate to an aqueous solution of a magnesium salt and saturating it with carbon dioxide.



$$MgCl_2 + 2NaHCO_3 + CO_2 + H_2O \rightarrow MgCO_3 \downarrow + 2NaCl + 2H_2CO_3$$

The carbonate precipitated from a magnesium salt with any soluble carbonate is the basic carbonate, $Mg(OH)_2.3MgCO_3.2H_2O$ called *magnesia alba*, and is used as a cosmetic, in medicines and in tooth powders. In the presence of ammonium chloride, magnesium carbonate is not precipitated.

It gives out carbon dioxide on heating and dissolves in acids. It is used for preparing other magnesium salts.

9. **Magnesium Chloride, $MgCl_2.6H_2O$.**—It is present in sea water and carnallite. It is prepared in the laboratory by dissolving magnesium oxide or carbonate in hydrochloric acid. On evaporation, the hexahydrate, $MgCl_2.6H_2O$ crystallizes out.

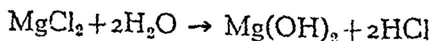
It is a colourless, crystalline, deliquescent substance soluble in water. On heating it loses water and hydrochloric acid.



$$MgCl_2.6H_2O \rightarrow MgO + 2HCl + 5H_2O$$

The anhydrous salt, therefore, cannot be prepared by heating the hydrate. It is obtained by heating it in a current of dry hydrochloric acid gas.

In solution, it hydrolyses to give hydrochloric acid especially at higher temperature which is the cause of corrosion in boilers when sea water is used.

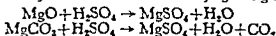


$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$$

Uses. (*i*) For making Sorel's cement. (*ii*) In cotton dressing.

10. **Magnesium Sulphate, Epsom Salt, $MgSO_4.7H_2O$.**—It is found in some mineral springs and has long been known and used as a purgative. It is prepared by dissolving magnesium oxide

or carbonate in dilute sulphuric acid and evaporating the solution when the heptahydrate crystallizes out as colourless efflorescent crystals. The anhydrous salt is obtained by igniting the hydrate.



$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$
$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2$$

It is manufactured by recrystallization of *kieserite*, $MgSO_4.H_2O$ found in the Stassfurt salt beds.

Uses. Epsom salt is used extensively—(*i*) As a purgative. (*ii*) In dyeing and tanning processes and in dressing cotton goods. (*iii*) As a reagent in the laboratory.

11. **Magnesium Nitrate, $Mg(NO_3)_2.6H_2O$.**—It is prepared in the laboratory by dissolving magnesium oxide or carbonate in ... the solution when hydrated ... It forms colourless deliques- ... It decomposes on heating. The anhydrous salt cannot, therefore, be prepared by heating the hydrated salt.



$$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$$

12. **Tests for Magnesium**

(*i*) *Charcoal cavity test.* Magnesium salts, when heated strongly in a charcoal cavity, leave a white residue. This when moistened with a drop of cobalt nitrate and heated changes to pink.

(*ii*) Magnesium salt solution is mixed with ammonium chloride and ammonium hydroxide and finally treated with a soluble phosphate when a white precipitate of magnesium ammonium phosphate is obtained. (*Note : Other alkaline earths and heavy metals must be absent for this test.*)

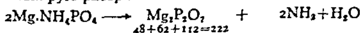


$$MgSO_4 + Na_2HPO_4 + NH_4OH \longrightarrow \underset{\text{White ppt.}}{Mg(NH_4)PO_4} + Na_2SO_4 + H_2O$$

(*iii*) *With sodium hydroxide solution*, soluble magnesium salts give white precipitate of the hydroxide soluble in excess of the reagent.

13. **Estimation of Magnesium.**—Precipitation of magnesium as *magnesium ammonium phosphate* is used for estimation ...

magnesium pyro-phosphate.



$$2Mg.NH_4PO_4 \longrightarrow \underset{48+62+112=222}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

From the weight of the residue left, percentage of magnesium can be calculated in the original salt. One molecule or 222 parts *by weight of pyrophosphate contain 2 atoms or* 48 parts by weight of magnesium.

$$\therefore \text{Percentage of magnesium} = \text{Wt. of residue} \times \frac{48}{222} \times \frac{100}{\text{Wt. of salt}}$$

14. **Historical.**—Lime was prepared by heating limestone used for mortar by the ancients. The name calcium was derived from the Latin *calx* (=lime). Davy was the first to prepare the metal by electrolytic method in 1808. The pure metal was, however, obtained by Moissan in 1898 by reduction of calcium iodide with metallic sodium.

15. **Occurrence.**—Calcium occurs in nature only in the combined state, as

(*i*) *Carbonate, e.g.*, limestone, iceland spar, marble, chalk and dolomite, $CaCO_3.MgCO_3$.

(*ii*) *Sulphate, e.g.*, gypsum, $CaSO_4.2H_2O$.

(*iii*) *Fluoride, e.g.*, fluorspar, CaF_2 and fluorapatite,

$$3Ca_3(PO_4)_2.CaF_2.$$

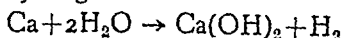
(*iv*) *Phosphate, e.g.*, phosphorite, $Ca_3(PO_4)_2$ and double salts.

Soluble calcium salts are present in sea water. Plants and animals need calcium salts for body building. Protective shells of marine animals are mainly calcium carbonate whereas bones and teeth are made of calcium phosphate.

16. **Preparation of Calcium.**—Metallic calcium is obtained by the electrolysis of a fused mixture (m.p. 644°) of calcium chloride (m.p. 744°) and calcium fluoride (m.p. 1378°) in a graphite crucible which serves as the anode. The cathode is a movable iron rod which is raised during electrolysis in such a way that only the extreme tip of the deposited calcium is in contact with the fused electrolyte. This prevents melting of the metal in the bath and enables us to isolate the metal in the solid state which otherwise is not light enough to float on the fused electrolyte.

17. **Properties of Calcium.**—(*i*) It is a silvery-white metal which is malleable and hard (nearly as hard as tin).

(*ii*) In moist air, it is slowly tarnished but decomposes water fairly rapidly giving hydrogen.



$$Ca+2H_2O \rightarrow Ca(OH)_2+H_2$$

(*iii*) It burns in air forming the oxide and a little *calcium nitride*, Ca_3N_2. With hydrogen it gives *calcium hydride*, CaH_2 on heating whereas with carbon it gives *calcium carbide*, CaC_2. With chlorine it gives calcium chloride, $CaCl_2$.

(*iv*) It liberates hydrogen from acids.

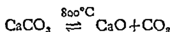
18. **Uses.** (*i*) As a drying agent in the preparation of absolute alcohol.

(*ii*) For absorbing air from castings.

(*iii*) For removing last traces of air from inert gases and to obtain high vacuum.

COMPOUNDS OF CALCIUM

19. Calcium Oxide, Quicklime, CaO (बिना बुझा चूना).—It is prepared on a commercial scale by burning limestone in specially designed kilns.



$$CaCO_3 \overset{800°C}{\rightleftharpoons} CaO+CO_2$$

The reaction being reversible, carbon dioxide should be removed to favour the forward reaction. Temperature should be kept low, because otherwise at a higher temperature fusible silicates will be produced by the interaction of lime and clay.

Previously and to some extent even now a mixture of limestone and fuel is heated in a kiln when we get lime contaminated with ash.

In modern continuous lime kilns (Fig. 54·2) fuel is burnt in separate fire boxes placed near the bottom when only hot gases rise up through limestone charged continuously from the top. Decomposition occurs and carbon dioxide is swept away by draft of air. Quicklime is being continuously removed from the bottom. The process is thus continuous.

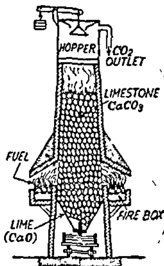


Fig. 54·2—Modern continuous lime kiln.

Properties. Lime is a white porous solid which is infusible and gives brilliant white *limelight* when heated in an oxy-hydrogen flame.

[illegible] becomes very hot. [illegible] (बुझा चूना) and consis[illegible] rocess is called *slaking* of lime.



$$CaO+H_2O \rightarrow Ca(OH)_2+15{,}000 \text{ calories.}$$

The paste of lime in water is called milk of lime whereas the filtered and clear solution is known lime water. Chemically either of these is calcium hydroxide.

[illegible] OCl_2. [illegible] with [illegible] gases [illegible] acid [illegible] ction with the dry gas.



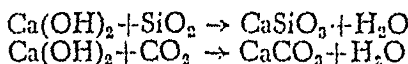
$$CaO+2HCl \rightarrow CaCl_2+H_2O$$

Uses. (*i*) For the manufacture of calcium carbide, cement, mortar and glass. (*ii*) In lime-light. (*iii*) For drying gases and alcohol. (*iv*) For preparing ammonia and soda-lime (lime soaked

in caustic soda solution). (*v*) As basic lining in furnaces. (*vi*) As slaked lime for manufacture of caustic soda, sodium carbonate, bleaching powder and basic calcium nitrate. (*vii*) As milk of lime in refining sugar and whitewashing. (*viii*) Lime water is used as a reagent in laboratory and in medicine.

20. Mortar.—A mixture of slaked lime, sand and water is known as *lime mortar*. Function of sand in it is to make the mass more porous, harder and to prevent excessive shrinkage which might result in cracks. It has been used as a building material for many centuries but how it sets to hard mass is not fully understood even now.

Loss of water by evaporation seems to be the main factor. Lime and sand also react to some extent though very slowly to give calcium silicate. At the same time carbon dioxide reacts with lime to give calcium carbonate.



$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3 + H_2O$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

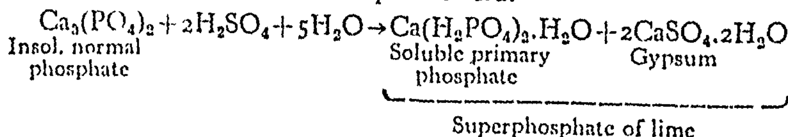
This view is supported by the fact that mortar becomes harder over a period of many years as the chemical changes occur in the centre of the mass.

Mortar to which cement has been added is harder and more waterproof. It is called *cement mortar*.

21. **Portland Cement.**—It is manufactured from limestone and clay. Powdered limestone and clay mixed in a suitable ratio are heated strongly in a cement kiln. The mass fuses to give clinker—hard particles about the size of peas. The clinker is mixed with 2-3 per cent of gypsum and ground to as fine a powder as possible when we get cement. This is sometimes called *hydraulic cement* because it has the property of setting and hardening under water. It is one of our most important materials today.

22. **Superphosphate of Lime, $Ca(H_2PO_4)_2$.**

Preparation. Superphosphate of lime is prepared on a commercial scale by treating calcium phosphate (phosphorite rock or bone-ash) with concentrated sulphuric acid.



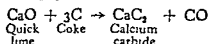
$$\underset{\text{Insol. normal phosphate}}{Ca_3(PO_4)_2} + 2H_2SO_4 + 5H_2O \rightarrow \underbrace{\underset{\text{Soluble primary phosphate}}{Ca(H_2PO_4)_2.H_2O} + \underset{\text{Gypsum}}{2CaSO_4.2H_2O}}_{\text{Superphosphate of lime}}$$

Calcium phosphate is thoroughly mixed with a calculated quantity of concentrated sulphuric acid in a mixer and dumped into a big chamber where it is allowed to remain for about 36 hours. Tht reaction being exothermic, the temperature rises about 100°C and the product finally solidifies to hard mass due to the formation of gypsum —$CaSO_4.2H_2O$. It is crushed to a fine powder and sold under the name superphosphate of lime.

Properties and Uses. The most important property of superphosphate of lime that is responsible for its use as a valuable

23. Calcium Carbide, CaC_2.

Preparation. Calcium carbide is commercially prepared by *heating strongly* a *mixture* of calcium oxide and powdered coke in an electric furnace (Fig. 54·3) at a temperature of over 2000°C.



$$\underset{\text{Quick lime}}{CaO} + \underset{\text{Coke}}{3C} \rightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

The charge is heated by the electric arc set up between the upper suspended graphite electrodes and blocks of graphite at the bottom which form the lower electrode. Calcium carbide produced is in the molten state and is tapped periodically from the tapping hole below or in the side.

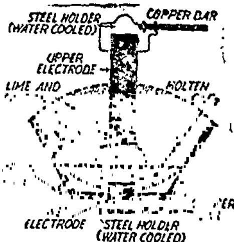
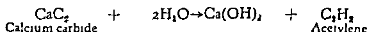


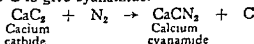
Fig. 54·3—Electric furnace for the commercial preparation of calcium carbide.

Properties. The commercial product is a hard crystalline mass with dark grey colour. With water it gives acetylene gas according to the reaction.



$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \rightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{C_2H_2}$$

With nitrogen it combines when heated under pressure at 1000—1100°C to give cyanamide.



$$\underset{\text{Cacium carbide}}{CaC_2} + N_2 \rightarrow \underset{\text{Calcium cyanamide}}{CaCN_2} + C$$

Uses. (i) As a source of acetylene used in oxy-acetylene blow-pipe, in acetylene lamps and in synthesis.

(ii) For manufacturing calcium cyanamide—a valuable fertilizer and source of commercial ammonia.

Estimates of Capacity and Production of Calcium Carbide in India
(in thousand tonnes)

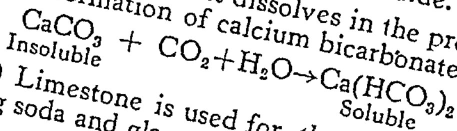
	1960-61	1965-66	1970-71	1975 76
Capacity	24	58	85	85
Production	10	55	80	80

24. Calcium Carbonate, $CaCO_3$.—Calcium carbonate is found in nature as :

(i) *Limestone* available in Kathiawar and Jabalpur.
(ii) *Marble* found in Rajasthan and near Jabalpur.
(iii) *Iceland spar, dolomite* and shells of sea animals.

In the laboratory, calcium carbonate (precipitated chalk) is precipitated by passing carbon dioxide through lime-water or adding sodium carbonate solution to calcium chloride.

It is insoluble in water but dissolves in the presence of carbon dioxide due to the formation of calcium bicarbonate.



$$\underset{\text{Insoluble}}{CaCO_3} + CO_2 + H_2O \rightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

Uses. (*i*) Limestone is used for the manufacture of lime, cement, washing soda and glass.

(*ii*) Marble is used for building purposes and also in the laboratory.

(*iii*) Chalk is used in paint whereas precipitated chalk is used in tooth pastes and powders.

25. **Calcium Sulphate, $CaSO_4$.**—It occurs as *Anhydrite*, $CaSO_4$ and *Gypsum*, $CaSO_4.2H_2O$. It is sparingly soluble in cold water and on heating its solubility decreases further. It dissolves in ammonium sulphate solution forming $CaSO_4.(NH_4)_2SO_4.H_2O$.

Gypsum loses water on heating at about 120°C to form the half hydrate, $CaSO_4.\frac{1}{2}H_2O$ or $2CaSO_4.H_2O$ which is called **Plaster of Paris.** When made into paste with a little water, plaster of Paris sets to a hard mass which expands with hardening. The final product of setting is $CaSO_4.2H_2O$ but setting is more complex a change than mere reversal of dehydration.

Gypsum when heated very strongly loses whole of its water of hydration. It does not set like plaster of Paris and gypsum is said to be *dead burnt*.

Uses. (*i*) Plaster of Paris finds use in making casts ar patterns. It is used in surgery for plastering of fractured part c he body and for preparing blackboard chalk.

(*ii*) Gypsum is used in the manufacture of cement and plaster Paris ; in agriculture and for impregnating filter papers.

26. **Calcium Chloride, $CaCl_2.6H_2O$.**—It occurs in sea ter and is obtained as a by-product in the ammonia soda process the manufacture of washing soda.

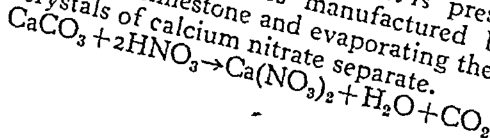
It is very deliquescent and on strong heating loses its water ystallization and the anhydrous salt is obtained.

Uses. (*i*) Fused calcium chloride is used for drying gases quids. With ammonia and alcohol it gives definite coms ($CaCl_2.8NH_3$ and $CaCl_2.4C_2H_5OH$ respectively). These , therefore, be dried with calcium chloride.

ii) It is also sprinkled on roads and keeps them wet.

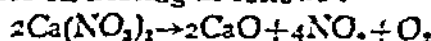
i) It is also used for making freezing mixtures.

Calcium Nitrite, $Ca(NO_3)_2$.—It is present in the soil similated by plants. It is manufactured by neutralizing ric acid with limestone and evaporating the solution when ent crystals of calcium nitrate separate.



$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$

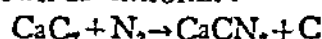
It decomposes on heating as follows :



$$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$$

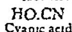
[illegible] sic calcium nitrate [illegible] and extensively [illegible]

28. **Calcium Cyanamide, CaNCN.**—It is prepared by passing nitrogen gas over crushed calcium carbide heated electrically at 1000—1100°C by carbon electrodes placed in drums of carbide. Calcium cyanamide mixed with graphite is formed as a dark grey mass known as 'nitrolim'.

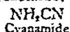


$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

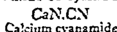
It is a derivative of cyanamide, the amide of cyanic acid.



HO.CN
Cyanic acid

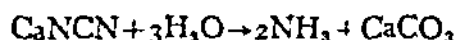


NH_2CN
Cyanamide



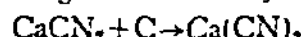
CaN.CN
Calcium cyanamide

When heated with water under pressure, calcium cyanamide gives ammonia and calcium carbonate.



$$CaNCN + 3H_2O \rightarrow 2NH_3 + CaCO_3$$

On fusing cyanamide alone or mixed with common salt in an electric furnace it gives calcium cyanide.



$$CaCN_2 + C \rightarrow Ca(CN)_2$$

Calcium cyanamide is used as a fertilizer.

29. **Bleaching Powder, Chloride of Lime, $CaOCl_2$.**—*See* page 2·107.

30. **Fertilizers**—Plants require compounds of more than a dozen different elements for healthy growth. Nitrogen, phosphorus and potassium are the big three among them and are most vital. Calcium, magnesium and sulphur are the little three which are essential but needed in smaller amounts. Several others needed in traces are : iron, manganese, copper, zinc, boron and iodine.

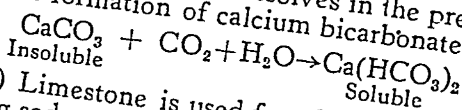
Growing plants obtain most of these nutrients from the soil. Since the soil does not contain an inexhaustible supply of these elements, we must add these nutrients to the soil in the form of manures or fertilizers. Different types of manures are : (i) Animal manures consisting of animal waste ; (ii) Plant manures obtained from decayed plants ; (iii) Chemical manures—various chemical *compounds containing the nutrient elements.*

[illegible] calcium nitrate [$Ca(NO_3)_2$ CaO], [illegible] $Ca(H_2PO_4)_2$ H_2O, Potassium chloride, Potassium sulphate and Potassium nitrate.

Fertilizers in India. The production of nitrogenous fertilizers during 1964 had increased to 224,579 tonnes from 219,275 tonnes in 1963, according to an annual report of the Ministry of Petroleum and Chemicals.

In the laboratory, calcium carbonate (precipitated chalk) is precipitated by passing carbon dioxide through lime-water or adding sodium carbonate solution to calcium chloride.

It is insoluble in water but dissolves in the presence of carbon dioxide due to the formation of calcium bicarbonate.



$$\underset{\text{Insoluble}}{CaCO_3} + CO_2 + H_2O \rightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

Uses. (*i*) Limestone is used for the manufacture of lime, cement, washing soda and glass.

(*ii*) Marble is used for building purposes and also in the laboratory.

(*iii*) Chalk is used in paint whereas precipitated chalk is used in tooth pastes and powders.

25. **Calcium Sulphate, $CaSO_4$.**—It occurs as *Anhydrite*, $CaSO_4$ and *Gypsum*, $CaSO_4.2H_2O$. It is sparingly soluble in cold water and on heating its solubility decreases further. It dissolves in ammonium sulphate solution forming $CaSO_4.(NH_4)_2SO_4.H_2O$.

Gypsum loses water on heating at about 120°C to form the half hydrate, $CaSO_4.\frac{1}{2}H_2O$ or $2CaSO_4.H_2O$ which is called ***Plaster of Paris***. When made into paste with a little water, plaster of Paris sets to a hard mass which expands with hardening. The final product of setting is $CaSO_4.2H_2O$ but setting is more complex a change than mere reversal of dehydration.

Gypsum when heated very strongly loses whole of its water of hydration. It does not set like plaster of Paris and gypsum is said to be *dead burnt*.

Uses. (*i*) Plaster of Paris finds use in making casts and patterns. It is used in surgery for plastering of fractured part of the body and for preparing blackboard chalk.

(*ii*) Gypsum is used in the manufacture of cement and plaster of Paris ; in agriculture and for impregnating filter papers.

26. **Calcium Chloride, $CaCl_2.6H_2O$.**—It occurs in sea water and is obtained as a by-product in the ammonia soda process for the manufacture of washing soda.

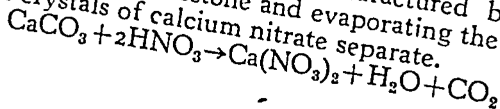
It is very deliquescent and on strong heating loses its water of crystallization and the anhydrous salt is obtained.

Uses. (*i*) Fused calcium chloride is used for drying gases nd liquids. With ammonia and alcohol it gives definite comounds ($CaCl_2.8NH_3$ and $CaCl_2.4C_2H_5OH$ respectively). These annot, therefore, be dried with calcium chloride.

(*ii*) It is also sprinkled on roads and keeps them wet.

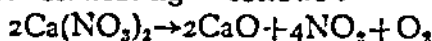
(*iii*) It is also used for making freezing mixtures.

27. **Calcium Nitrite, $Ca(NO_3)_2$.**—It is present in the soil d is assimilated by plants. It is manufactured by neutralizing ute nitric acid with limestone and evaporating the solution when quescent crystals of calcium nitrate separate.



$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$

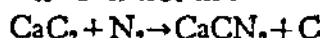
It decomposes on heating as follows :



$$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$$

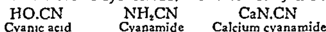
When mixed with lime calcium nitrate gives basic calcium nitrate, $Ca(NO_3)_2.CaO$ called Norwegian saltpetre and extensively employed in agriculture as a fertilizer.

28. **Calcium Cyanamide, CaNCN.**—It is prepared by passing nitrogen gas over crushed calcium carbide heated electrically at 1000—1100°C by carbon electrodes placed in drums of carbide. Calcium cyanamide mixed with graphite is formed as a dark grey mass known as 'nitrolim'.



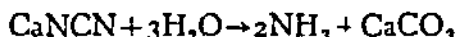
$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

It is a derivative of cyanamide, the amide of cyanic acid.



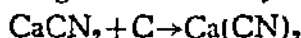
HO.CN	NH_2CN	CaN.CN
Cyanic acid	Cyanamide	Calcium cyanamide

When heated with water under pressure, calcium cyanamide gives ammonia and calcium carbonate.



$$CaNCN + 3H_2O \rightarrow 2NH_3 + CaCO_3$$

On fusing cyanamide alone or mixed with common salt in an electric furnace it gives calcium cyanide.



$$CaCN_2 + C \rightarrow Ca(CN)_2$$

Calcium cyanamide is used as a fertilizer.

29. **Bleaching Powder, Chloride of Lime, $CaOCl_2$.**— *See* page 2·107.

30. **Fertilizers**—Plants require compounds of more than a dozen different elements for healthy growth. Nitrogen, phosphorus and potassium are the big three among them and are most vital. Calcium, magnesium and sulphur are the little three which are essential but needed in smaller amounts. Several others needed in traces are : iron, manganese, copper, zinc, boron and iodine.

Growing plants obtain most of these nutrients from the soil. Since the soil does not contain an inexhaustible supply of these elements, we must add these nutrients to the soil in the form of manures or fertilizers. Different types of manures are : (i) Animal manures consisting of animal waste ; (ii) Plant manures obtained from decayed plants ; (iii) Chemical manures—various chemical compounds containing the nutrient elements.

The chemical manures must be soluble in the soil moisture to make the nutrient elements more easily available to the plants. Different substances used for the purpose are : Calcium cyanamide, Ammonium sulphate, Sodium nitrate (Chile saltpetre), Basic calcium nitrate $[Ca(NO_3)_2.CaO]$, Superphosphate of lime, $Ca(H_2PO_4)_2.H_2O$, Potassium chloride, Potassium sulphate and Potassium nitrate.

Fertilizers in India. The production of nitrogenous fertilizers during 1964 had increased to 224,579 tonnes from 219,275 tonnes in 1963, according to an annual report of the Ministry of Petroleum and Chemicals.

Against the production target of one million tonnes by the end of the third Plan, installed capacity at present is only 386,550 tonnes.

When the Fertilizer Corporation would complete all its five new projects—Trombay, Namrup, Gorakhpur, Durgapur and Korba—the Corporation alone would have developed an overall production capacity of 790,500 tonnes of fertilizers—637,000 tonnes of nitrogen and 153,500 tonnes of phosphate. Presently the Sindri and Nangal units of the Corporation have a capacity of 197,000 tonnes of nitrogen only.

In the private sector, five projects had been licensed with a total capacity of 516,000 tonnes of nitrogen. Shriram Fertilizers, Kota, has started production and is manufacturing urea. Tata Fertilizers is another concern which got a licence in 1971.

To achieve the fourth Plan target of 2 million tonnes of nitrogen, the Government had requested Bechtel Corporation, U.S.A., to undertake a feasibility study to set up five more plants.

Sindri Fertilizers Company has submitted a Rs. 15-crore plan to the Fertilizer Corporation of India and the Ministry of Petroleum and Chemicals to increase production of Sindri.

The increase is sought to be achieved by raising production at the new ammonia plant to full capacity and by installing additional plants to produce above 100,000 tonnes of phosphoric fertilizers.

The proposed installations are a sulphuric acid plant costing Rs. 375·86 lakhs, a phosphoric acid plant costing Rs. 871·55 lakhs and an ammonium nitrate plant estimated to cost Rs. 30·19 lakhs.

The superphosphate industry, which consumes over 20 per cent of sulphuric acid manufactured in India, cannot be expanded to any considerable extent owing to the acute shortage of sulphur. Methods for the manufacture of dicalcium phosphate by the action of hydrochloric acid on calcium phosphate from Trichinapali are being developed. Dicalcium phosphate is a better fertilizer.

Estimates of Capacity and Production of Fertilizers in India
(in thousand tonnes)

	1960-61	1965-66	1970-71	1975-76
Nitrogenous Capacity	161	640	2,000	3,500
Production	99	500	1,750	3,000
Phosphate Capacity	58	270	1,250	2,000
Production	54	200	750	2,700

31. **Tests for Calcium.**—(*i*) *Flame test.* A paste of calcium salt in concentrated hydrochloric acid imparts brick-red colour to the flame which is invisible through blue glass.

(*ii*) *With ammonium carbonate.* The solution of calcium salt containing ammonium chloride and ammonium hydroxide, gives a white precipitate with ammonium carbonate. The precipitate is soluble in dilute acids.

(*iii*) *With ammonium oxalate*, calcium salts give white crystalline precipitate of calcium oxalate insoluble in acetic acid but soluble in dilute nitric acid.

Note. Both barium and strontium salts give precipitate with ammonium oxalate. Hence this is a confirmatory test for calcium only when absence of barium and strontium has already been shown.

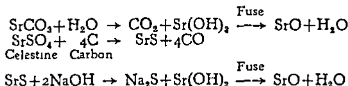
STRONTIUM ACID ITS COMPOUNDS

32. **Strontium.**—It occurs in the combined state, not free, as *Strontianite*, $SrCO_3$ and *Celestine*, $SrSO_4$. It is prepared by the electrolysis of fused strontium chloride as described under calcium.

Properties. It resembles calcium in both its physical and chemical properties. For example, this is also a silvery-white, soft metal which is malleable and ductile. It is also a light metal (Sp. Gr. 2·5). It is comparatively more electropositive than calcium.

33. Compounds of Strontium.

Strontium Oxide, Strontia, SrO. It is prepared by heating the carbonate or nitrate. It is obtained on a large scale by heating the carbonate in superheated steam or by reducing celestine with carbon and treating the fused mass (the sulphide) with caustic soda. Strontium hydroxide obtained in either case is ignited to get the oxide.



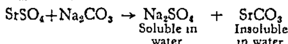
$$SrCO_3 + H_2O \rightarrow CO_2 + Sr(OH)_2 \xrightarrow{\text{Fuse}} SrO + H_2O$$

$$\underset{\text{Celestine}}{SrSO_4} + \underset{\text{Carbon}}{4C} \rightarrow SrS + 4CO$$

$$SrS + 2NaOH \rightarrow Na_2S + Sr(OH)_2 \xrightarrow{\text{Fuse}} SrO + H_2O$$

It is a white powder which slakes on addition of water just like quicklime. It is used in the recovery of sugar from molasses.

Strontium carbonate, $SrCO_3$. It occurs in nature as strontianite and is also prepared commercially from celestine by fusion with sodium carbonate.



$$SrSO_4 + Na_2CO_3 \rightarrow \underset{\text{Soluble in water}}{Na_2SO_4} + \underset{\text{Insoluble in water}}{SrCO_3}$$

It resembles calcium carbonate but decomposes on heating not so readily as calcium carbonate.

Strontium chloride, $SrCl_2.6H_2O$. It is prepared by dissolv- [illegible] nate in dilute hydrochloric [illegible] very soluble in water but [illegible]

Strontium sulphate, $SrSO_4$. It occurs in nature as *celestine* and can be precipitated by adding a soluble sulphate to any strontium salt solution as it is insoluble in water.

Str [illegible] ing stron [illegible] evaporati [illegible] lizes out. It is soluble in water though less than calcium nitrate. It is used in pyrotechny for getting 'red fires'.

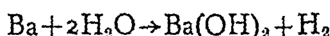
34. Tests for Strontium.—(i) *Flame test.* A paste of strontium salt in concentrated hydrochloric acid imparts crimson colour to flame which is visible through blue glass (*cf.*, calcium).

(ii) *With saturated calcium sulphate solution* it gives a white precipitate of strontium sulphate formed slowly in cold but more rapidly on boiling (*cf.*, barium).

BARIUM AND ITS COMPOUNDS

35. **Barium.**—Barium occurs only in the combined state as *Barytes or Heavy spar*, $BaSO_4$ and *Witherite*, $BaCO_3$. It is prepared by the electrolysis of its fused chloride using mercury cathode. Metal liberated at the cathode forms barium amalgam which is distilled in vacuo when mercury distils over and barium is left.

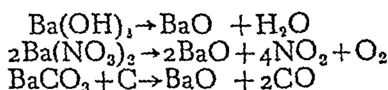
Properties. In its properties barium resembles calcium and strontium. It is a silvery-white metal, soft, light (SP. Gr. 3·8) and malleable. It melts at 850°C. Chemically it is more active than calcium and strontium. It burns in air forming oxide and in nitrogen forming the nitride. It decomposes water forming hydroxide.



$$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$$

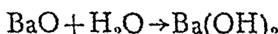
36. **Compounds of Barium.**

Barium oxide, Baryta, BaO. It is often prepared by decomposing barium nitrate or hydroxide at red heat, or heating a mixture of barium carbonate with carbon.



$$Ba(OH)_2 \rightarrow BaO + H_2O$$
$$2Ba(NO_3)_2 \rightarrow 2BaO + 4NO_2 + O_2$$
$$BaCO_3 + C \rightarrow BaO + 2CO$$

It is a white powder which slakes on adding water with the evolution of much heat



$$BaO + H_2O \rightarrow Ba(OH)_2$$

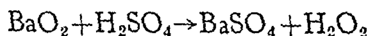
When heated with air it forms barium peroxide which decomposes again at a higher temperature liberating oxygen.



$$2BaO + O_2 \rightleftharpoons 2BaO_2$$

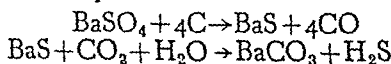
This reaction is made use of in the manufacture of oxygen by *Brin's process.*

Barium peroxide, BaO_2. It is prepared from baryta as given above. It is a white powder insoluble in water. A paste of barium peroxide in ice-cold water gives hydrogen peroxide when treated with ice-cold dilute acid or carbon dioxide.



$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

Barium carbonate, $BaCO_3$. It is found native as witherite. From heavy spar it is prepared by its reduction with carbon and treating the barium sulphide obtained with carbon dioxide.



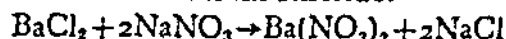
$$BaSO_4 + 4C \rightarrow BaS + 4CO$$
$$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S$$

It is a white powder insoluble in water. It decomposes on heating but at a much higher temperature than needed for decomposing calcium carbonate.



$$BaCO_3 \xrightarrow{1450^\circ} BaO + CO_2$$

Barium nitrate, $Ba(NO_3)_2$. It is usually prepared by mixing solution of sodium nitrate and barium chloride.



$$BaCl_2 + 2NaNO_3 \rightarrow Ba(NO_3)_2 + 2NaCl$$

It gives colourless crystals soluble in water and is used in fireworks for making 'green fires', also in preparing the oxide.

Barium sulphate, $BaSO_4$. It is found native as *barytes* and may be prepared by adding any soluble sulphate to a soluble barium salt.

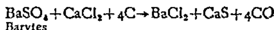
It forms a white powder, insoluble in water and stable towards heat and other common reagents.

Uses. (i) As a white pigment either as such or mixed with zinc sulphide under the name *lithopone.*

(ii) As a filler in rubber and paper industry.

(iii) As a source of other barium compounds.

Barium chloride, $BaCl_2.2H_2O$. It is prepared commercially by fusing barytes, calcium chloride and coke.



$$\underset{\text{Barytes}}{BaSO_4} + CaCl_2 + 4C \rightarrow BaCl_2 + CaS + 4CO$$

The fused mass is extracted with water and evaporated when hydrated crystals of the salt are deposited.

It is a colourless crystalline substance and is not deliquescent (*cf.*, $CaCl_2$). It is extensively used in analysis for the detection and estimation of sulphate radical.

37. **Tests for Barium.**

(i) *Flame test.* Barium salts impart an apple green colour to flame.

(ii) *Chromate test.* A soluble chromate gives a yellow precipitate of barium chromate with any soluble barium salt.

(iii) *Sulphate test.* Barium salts give a white precipitate of barium sulphate insoluble in concentrated hydrochloric acid when treated with any soluble sulphate.

TEST YOURSELF ON THESE REACTIONS

Write equations for these reactions, if any, between .

1. Magnesium + (i) Oxygen (burning , (ii) Nitrogen (burning), (iii) Carbon dioxide (burning), (iv) Boiling water, (v) Dil hydrochloric acid and Sulphuric acid, (vi) Nitric acid.

2. Action of heat on (i) Magnesium nitrate, (ii) $MgCl_2.6H_2O$, (iii) $MgNH_4PO_4$.

3. Calcium carbide + (i) Water, (ii) Nitrogen.

4. Barium peroxide + Dil. Sulphuric acid

QUESTIONS

Essay-Type Questions

1. (a) What are the chief ores of magnesium ? Describe one method of extraction of the metal.

(b) Starting with magnesium, how will you prepare its oxide, chloride, sulphate and hydroxide ? *(Delhi Prep 1969 ; U.P. Board 1969)*

2. "Calcium, strontium and barium are said to form a family of metals." *Justify clearly the statement from a comparative study of these metals* and their compounds.

3. Compare and contrast the general properties and reactions of alkali metals and alkaline earth metals. Why are they so called ?

Describe the tests by which you would distinguish between a potassium salt and a calcium salt.

4. Give the commercial preparation, important properties and uses of the following compounds :

(*a*) Plaster of Paris. (*Punjab Inter. 1960 Supp. ; Delhi H.S. 1971, 66, 60*)

(*b*) Calcium carbide. (*Delhi H.S. 1971*)

(*c*) Superphosphate of lime. (*Delhi H.S. 1970, 68, 65, 63, 61*)

(*d*) Epsom salt. (*Punjab H.S. 1963 ; Delhi Prep. 1960*)

(*e*) Lime. (*Delhi H.S. 1968 ; Kashmir Inter. 1960*)

(*f*) Portland cement.

(*g*) Anhydrous magnesium chloride.

(*h*) Calcium cyanamide.

5. By what laboratory tests would you distinguish between :

(*a*) Magnesium chloride and barium chloride.

(*b*) Calcium and barium chloride ?

6. What are the elements required by plant life for its nutrition ? What salts are used to supply these elements ? Give in detail the method of manufacture of one fertilizer.

Test Your Understanding

7. Fill in the blanks in the following :

(*i*) Alkaline earth metals belong to sub-group......of the periodic table.

(*ii*) Three main elements required by plants are......,......and......

(*iii*) ......is being manufactured at Sindri......at Nangal and......at Kota.

(*iv*) Calcium cyanamide is manufactured by heating......under pressure at 1000—1100°C in a current of......

(*v*) Cement is manufactured from......and......

KEY

(*i*) IIA ; (*ii*) Nitrogen, phosphorus, potassium ; (*iii*) Ammonium sulphate, ammonium *nitrate, urea* ; (*iv*) *Calcium carbide, nitrogen* ; (*v*) Limestone, clay.

THE ZINC GROUP– METALS Zn, Cd, Hg
CONSTITUTE GROUP II B OF THE PERIODIC TABLE

1. THEY HAVE SIMILAR CONFIGURATION.
2. THEY OCCUR AS SULPHIDES.
3. THEIR OXIDES CAN BE REDUCED WITH CARBON.
4. NO ACTION OF AIR & WATER IN COLD
5. THEY GIVE NO FLAME TEST.
6. THEIR COMPOUNDS [MSO_4, $M(OH)_2$, BASIC CARBONATES & COLORIDES] ARE SIMILAR.
7. THEIR RECTIVITY DECREASES FROM Zn TO Hg.

	VIII	IB	IIB	IIIA	IVA	
				B	C	
				Al	Si	
	Fe Co Ni	Cu	Zn	Ga	Ge	.
		Ag	Cd			
		Au	Hg			

55

The Zinc Group

1. **General.**—The zinc group includes the elements zinc, cadmium and mercury which constitute sub-group II B of the periodic table. That they form a family of closely related elements is shown by their general characteristics as given below :

(*i*) They all have two electrons in their valency shell (*see* table below) and are, therefore, *divalent*.

Element	At. wt.	At. No.	Electronic configuration	Specific gravity	Melting point	Boiling point
Zinc	65·38	30	2, 8, 18, 2	7·14	419·4°C	907°C
Cadmium	112·24	48	2, 8, 18, 18, 2	8·64	320 9	767
Mercury	200 06	80	2, 8, 18, 32, 18, 2	13 6	− 38 9	357

(*ii*) They occur as sulphides and their oxides being less basic can be easily reduced with carbon (*cf*., alkaline earth metal oxides which are strongly basic).

(*iii*) They are silver-white metals with low melting and boiling points.

(*iv*) They are tarnished in air and have no action on water at ordinary temperature.

(*v*) All of them give soluble *sulphates* which are decomposed by heat ; *hydroxides* which are insoluble and *chlorides* which are volatile and deliquescent.

(*vi*) They all give basic carbonates and basic chlorides.

(*vii*) Their compounds do not impart any characteristic colour to flame (*cf*., alkaline earth metals).

(*viii*) Their chemical activity decreases with the rise in atomic weight.

Magnesium resembles Zinc. For example :

(*i*) Both give sulphates which are isomorphous and soluble in water.

(*ii*) Both are not tarnished in dry air.

(*iii*) Both have no action on water at ordinary temperature.

(*iv*) Both do not impart any colour to flame.

(*v*) Both form basic carbonates.

Mercury differs from other members of the Zinc group. For example :

(*i*) It gives two series of salts, mercurous and mercuric.

(*ii*) It is weakly electropositive and does not displace hydrogen from dilute acids.

(*iii*) It is liquid at ordinary temperature.

On the other hand, it is found to resemble copper in many respects.

ZINC

2. **Historical and Occurrence.**—The ancients used an alloy of zinc and copper not very different from brass, long, long ago without knowing its actual composition.

The chief ores of zinc are : (*i*) *Zinc blende*—ZnS, (*ii*) *Calamine*—$ZnCO_3$, (*iii*) *Zincite*—ZnO, and (*iv*) *Franklinite*—$ZnO.Fe_2O_3$, the first two being more abundant.

Zinc deposits are known to exist in Zawar mines in Rajasthan. These are under lease to the Metal Corporation of India.

Estimates of Capacity and Production of Zinc Metal in India
(*in thousand tonnes*)

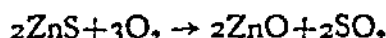
	1960-61	1965-66	1970-71	1975-76
Zinc ingots				
Capacity	...	18·4	60	100
Production	...	18·4	60	100
Zinc sheets				
Capacity	5·9	7	20	30
Production	5·9	7	20	30

3. **Reduction Process for the Extraction of Zinc.**—The reduction process for the extraction of the metal from its ores involves the following steps :

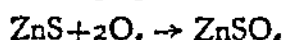
(1) **Crushing and Concentration.** The ore is crushed and finely powdered in ball mills and concentrated first by *Gravity Process* and then by *Froth Flotation Process*. Iron oxide, if

present as impurity, is removed by *electromagnetic separation* (*for details of these processes see page 2·288*).

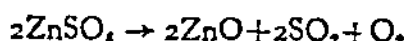
(2) **Roasting.** The concentrated ore is roasted at about 900°C in excess of air when zinc sulphide or any zinc sulphate formed by its oxidation changes to zinc oxide.



$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

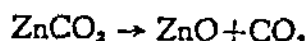


$$ZnS + 2O_2 \rightarrow ZnSO_4$$



$$2ZnSO_4 \rightarrow 2ZnO + 2SO_2 + O_2$$

Calamine, if used for the extraction of zinc, needs only calcination when it forms zinc oxide.



$$ZnCO_3 \rightarrow ZnO + CO_2$$

(3) **Reduction.** (*a*) *Belgian Process.* The roasted ore (ZnO) is next mixed with half its weight of carbon (powdered coal or coke) and taken in fire clay retorts which consist of bottle-shaped fire clay tubes (about 1 m. in length and 20 cm. in diameter as given in Fig. 55·1) closed at one end and fitted with earthenware condensers at their mouths. These are heated strongly in a gas fired furnace working on the regenerative principle of heat economy. Carbon monoxide formed by reduction of zinc oxide [ZnO+C→Zn+CO] burns at the mouth of the condenser with a flame which is coloured yellow by the slow vaporization of salt. If the colour of the flame changes to green due to burning of zinc vapour, a "prolong" made of sheet iron is slipped on the mouth of the condenser. This helps in completing the condensation.

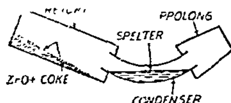


Fig. 55·1—Fire-clay retort with a prolong used in the Belgian process.

The metal distils off and condenses in these prolongs and ... is *zinc dust* (powder mixed with ... metal. The liquid solidified in

(*b*) *Silesian Process.* In this Silesian process the fire-clay retorts used are D-shaped and these are heated in a muffle furnace.

(*c*) *Vertical Retort Process.* In this case the roasted ore with powdered coal or coke is made into small briquettes and heated in a vertical retort. The retort is placed in a heating jacket

and heated by burning a fuel gas in the jacket (Fig. 55·2). Zinc oxide is reduced to zinc which vaporizes. The vapours of zinc escape near the top and condense in the condenser to give zinc spelter. The fresh charge is added through the charging door and the waste residue in the retort is constantly moving out with the help of an automatic screw conveyor fitted in the bottom. Thus the process is a continuous one.

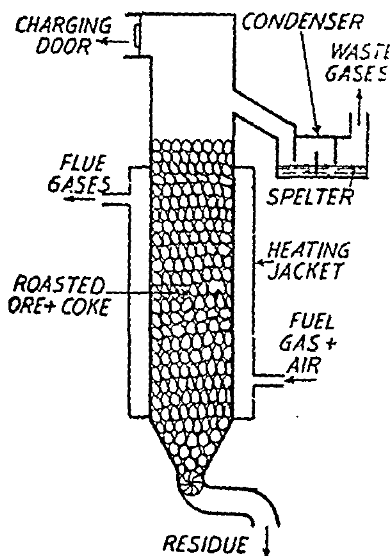


Fig. 55·2—Continuous vertical retort process.

(4) **Purification.** Commercial zinc contains 1·3% of lead, 0·1% of iron with traces of cadmium and arsenic. This may be purified by :

(*a*) **Liquation.** Crude zinc is melted on the sloping hearth of a reverberatory furnace when molten zinc flows down and non-fusible impurities are left behind.

(*b*) **Repeated distillation.** On heating zinc vaporizes and the vapour on cooling give zinc dust. Impurities are left behind.

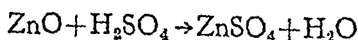
(*c*) **Electrolytic Purification.** Very pure zinc is obtained electrolytically. Impure zinc is made the anode and pure zinc plates are made the cathode in an electrolytic cell with zinc sulphate and a little sulphuric acid as electrolyte. On passing electric current pure zinc from the electrolyte is deposited on the cathode which grows in size. An equal amount of zinc passes into solution from the anode which dwindles in size.

4. **Electrolytic Process for the Extraction of Zinc.**—Zinc is also extracted from its ores by an electrolytic process. The different steps involved are :

(*i*) **Crushing and Concentration.** (*See under Reduction Process.*)

(*ii*) **Roasting.** The concentrated ore is roasted at moderate temperature when zinc sulphide is oxidized mainly to zinc sulphate. Some zinc oxide is also obtained (*see under Reduction Process*).

(*iii*) **Leaching with sulphuric acid.** The roasted ore is leached with sulphuric acid when zinc oxide is converted into zinc sulphate.



$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

(*iv*) **Precipitation of Impurities.** The solution obtained by leaching of roasted ore with sulphuric acid contains impurities like copper, cadmium, arsenic, antimony, manganese, aluminium, and iron. It is treated with milk of lime when iron, aluminium, arsenic

and antimony are precipitated. Manganese, if any, is oxidised by blowing in air. It is precipitated as hydrated oxide. It is next treated with zinc dust which liberates the less active metals, *e.g.*, copper, cadmium.

(*v*) **Electrolysis.** The purified zinc sulphate solution is electrolysed using high current density when zinc is deposited on [illegible] and stripped off by melting. [illegible] ...lting point of aluminium is [illegible] electrolytic bath is used again for leaching the roasted ore in (*iii*). Electrolytic zinc, that is 99·9 per cent pure, is prepared for making brass and other alloys because of its high purity.

5. **Properties of Zinc.**

(*a*) **Physical.** Metallic zinc is bluish-white in colour. It is somewhat brittle at room temperature but becomes malleable and ductile between 100°C and 150°C. Metal rolled into sheets and drawn into wire between these temperatures does not become brittle on cooling. Its physical constants are given on page 2·351. When molten zinc is poured on cold water, granulated zinc is formed.

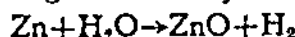
(*b*) **Chemical.** (*i*) It is a divalent electropositive metal.

(*ii*) *Action of air.* Dry air at room temperature has no action on zinc. A protective coating of basic zinc carbonate is formed on the surface in moist air, it burns with a bluish-white flame and forms zinc oxide called *Philosopher's wool.*



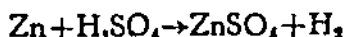
$$2Zn + O_2 \rightarrow 2ZnO$$

(*iii*) *Action of water.* Pure zinc has no action on water. Zinc-copper couple decomposes water liberating hydrogen. Impure zinc decomposes boiling water slowly and steam quickly.



$$Zn + H_2O \rightarrow ZnO + H_2$$

(*iv*) *Action of acids.* Chemically pure zinc is attacked very slowly by acids, but impure zinc reacts with ordinary acids rapidly. It liberates hydrogen from dilute hydrochloric or sulphuric acid.



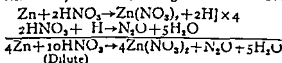
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

With hot concentrated sulphuric acid it gives sulphur dioxide.



$$Zn + 2H_2SO_4 \rightarrow ZnSO_4 + SO_2 + 2H_2O$$

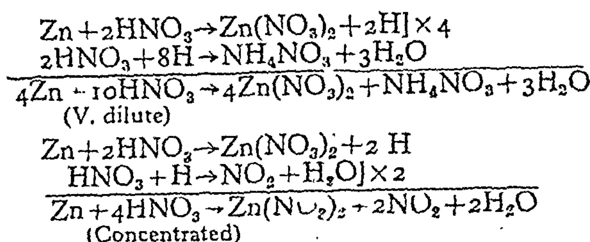
It reacts with dilute nitric acid liberating nitrous oxide, N_2O whereas ammonium nitrate is produced with very dilute acid. With concentrated nitric acid, however, nitrogen dioxide is evolved.



$$[Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + 2H] \times 4$$

$$2HNO_3 + H \rightarrow N_2O + 5H_2O$$

$$\underset{\text{(Dilute)}}{4Zn + 10HNO_3} \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$



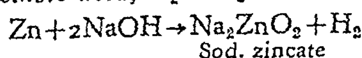
$$\begin{array}{l} Zn+2HNO_3 \rightarrow Zn(NO_3)_2+2H] \times 4 \\ 2HNO_3+8H \rightarrow NH_4NO_3+3H_2O \\ \hline 4Zn+10HNO_3 \rightarrow 4Zn(NO_3)_2+NH_4NO_3+3H_2O \end{array}$$

(V. dilute)

$$\begin{array}{l} Zn+2HNO_3 \rightarrow Zn(NO_3)_2+2H \\ HNO_3+H \rightarrow NO_2+H_2O] \times 2 \\ \hline Zn+4HNO_3 \rightarrow Zn(NO_3)_2+2NO_2+2H_2O \end{array}$$

(Concentrated)

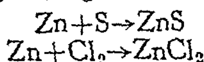
(*v*) *Action of alkalis.* Caustic alkalis react with zinc and se free hydrogen gas. Soluble zincates are formed and may be con sidered as salts of *zincic acid,* H_2ZnO_2.



$$Zn+2NaOH \rightarrow Na_2ZnO_2+H_2$$

Sod. zincate

(*vi*) *Action of sulphur and halogens.* Zinc combines directl with sulphur and halogens, *e.g.*,



$$Zn+S \rightarrow ZnS$$
$$Zn+Cl_2 \rightarrow ZnCl_2$$

(*vii*) Zinc salts are all poisonous. Acidic foods must not, there fore, be stored in galvanized iron containers. Zinc salts are know to form soluble complexes with ammonia, *e.g.*, $Zn(NH_3)_4SO_4$.

6. Uses of Zinc.—(1) Large quantities of zinc are used fo galvanizing iron. *Galvanizing is the art of depositing a thin laye of zinc on iron sheets to increase their life by protecting them fro rusting.*

The metal is thoroughly cleaned by pickling it in an acid bath. This removes any oxide film or tarnish on the surface. This is then coated with zinc by one of the following three methods :

(*i*) *By dipping.* Iron sheets are dipped in molten zinc and then passed through hot rollers when the superfluous zinc sticking to them is removed and a thin uniform coating is obtained. These are used for making bath tubs, buckets, utensils, roofings, gutters, etc. Iron wire is galvanized by pulling it through a bath of molten zinc.

(*ii*) *By plating.* In some cases a thin layer of zinc is deposited electrolytically. The article is made the cathode in an acidified zinc sulphate bath and a zinc rod is made the anode.

(*iii*) *By sherardizing.* In this process zinc dust is heated strongly when it vaporises and vapours of zinc are allowed to condense on the metallic surface to be coated with zinc.

(2) In making alloys, *e.g.*, brass, bronze and German silver (*see* page 2·321).

(3) In the metallurgy of gold and silver by the *cyanide process.*

(4) In the desilverization of lead by Parke's process.

(5) As the cathode container in making dry cells.

(6) Zinc dust is used as an important reducing agent in the manufacture of perfumes, synthetic drugs and dyestuffs.

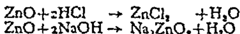
COMPOUNDS OF ZINC

7. **Zinc Oxide.**—It is formed when zinc carbonate, nitrate or hydroxide is strongly heated, but it is prepared by burning zinc.



$$2Zn + O_2 \rightarrow 2ZnO$$

It is a white powder commonly known as Philosopher's wool. It changes to yellow on heating. Being an amphoteric oxide, it dissolves both in acids and alkalis to give zinc salts and zincates respectively.



$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$
$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$

It is used as a white paint base and is called zinc *white* or *Chinese white*. It does not blacken with hydrogen sulphide like white lead and is, therefore, preferred. It is also used as a filler in rubber for automobile tyres, in oil cloth, in medicine (zinc ointment), elastoplast, for glazes and enamels.

8. Zinc Sulphate, White Vitriol $ZnSO_4.7H_2O$. Zinc [illegible]

[illegible]

It is a white crystalline solid used (i) in preserving hides, (ii) as mordant in calico-printing, (iii) in medicine as eye-lotion, and (iv) in making *lithopone*, a paint base.

9. **Zinc Sulphide.**—The sulphide of zinc is interesting being the only ordinary sulphide white in colour.

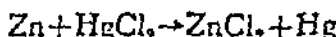
Lithopone is a mixture of zinc sulphide and barium sulphate (both white) precipitated by mixing solutions of barium sulphide and zinc sulphate.



$$BaS + ZnSO_4 \rightarrow BaSO_4 \downarrow + ZnS \downarrow$$

It is an important paint base as it does not darken in air containing hydrogen sulphide.

10. **Zinc Chloride, $ZnCl_2$.**—Anhydrous zinc chloride is obtained by passing chlorine or hydrogen chloride over heated zinc or distilling zinc with mercuric chloride.



$$Zn + HgCl_2 \rightarrow ZnCl_2 + Hg$$

Zinc chloride solution is obtained by dissolving the metal, its oxide or carbonate in hydrochloric acid. It gives $ZnCl_2.H_2O$ [illegible] hydrochloric [illegible] obtained [illegible]

It is white [illegible] g wood, e.g. rail-road ties and [illegible] oxide [illegible] water, a paste of [illegible] a hard mass and is used as a cement. It is used as a [illegible] soldering.

A concentrated solution of zinc chloride attacks wood fibre to give cellulose hydrate which may be moulded into any desired shape and dried. The product is called fireboard or vulcanized fibre and is used in making boxes, pails, trays and insulating materials.

It is an important dehydrating agent in organic chemistry and is used in dry cells.

11. **Zinc Carbonate.**—It occurs native as calamine. When a soluble zinc salt is treated with sodium carbonate, a basic carbonate with variable composition is precipitated. Sodium bicarbonate however, precipitates the normal salt.

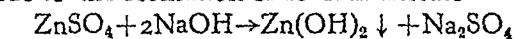


$$ZnSO_4+2NaHCO_3 \rightarrow ZnCO_3+Na_2SO_4+CO_2+H_2O$$

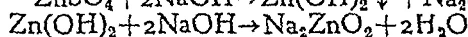
12. **Tests of Zinc.**—(*i*) *Charcoal cavity test.* On heating the salt with fusion mixture in a charcoal cavity, the residue is yellow when hot and white when cold. If this is moistened with a drop of cobalt nitrate and heated, residue is green due to the formation of ZnO.CoO, a double oxide.

(*ii*) An ammoniacal solution of a zinc salt containing ammonium chloride gives a white precipitate of zinc sulphide when hydrogen sulphide is bubbled through it.

(*iii*) The aqueous solution of zinc salt gives a white precipitate with ammonium or sodium hydroxide, soluble in excess of sodium hydroxide due to the formation of sodium zincate.



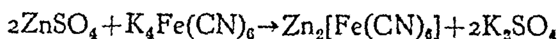
$$ZnSO_4+2NaOH \rightarrow Zn(OH)_2\downarrow+Na_2SO_4$$



$$Zn(OH)_2+2NaOH \rightarrow Na_2ZnO_2+2H_2O$$

(or H_2ZnO_2)

(*iv*) *Ferrocyanide test.* With potassium ferrocyanide, zinc salt precipitates zinc ferrocyanide, a white precipitate insoluble in dilute hydrochloric acid.



$$2ZnSO_4+K_4Fe(CN)_6 \rightarrow Zn_2[Fe(CN)_6]+2K_2SO_4$$

(*v*) *Ferricyanide test.* Soluble zinc salts give an orange precipitate of zinc ferricyanide when treated with potassium ferricyanide.

MERCURY

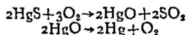
13. **Historical.**—Mercury was one of the metals known to the ancient Chinese and Hindus and is named after the planet by the same name. Aristotle refers to it as *quick silver* and the present symbol, Hg comes from the word *Hydrargyrum* derived from *hydroargyros* (liquid silver).

14. **Occurrence.**—Mercury sometimes occurs free as small globules scattered through rock although the principal ore of mercury is a red sulphide mineral called **cinnabar**, HgS. The bulk of the world's supply of mercury comes from Italy, Spain and the U.S.A.

15. **Extraction.**—The extraction of mercury from cinnabar involves the following steps :

(*i*) **Crushing and concentration.** The ore is crushed and finely powdered in ball mills and then concentrated by *Froth Flotation Process* (*see* page 2·287).

(*ii*) **Combined Roasting and Distillation.** The concentrated ore is placed on the perforated arches and heated by the flames rising from the furnace below (Fig. 55·3). Mercuric oxide first formed by oxidation of cinnabar, decomposes at about 300°C to give mercury.


$$2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$$
$$2HgO \rightarrow 2Hg + O_2$$

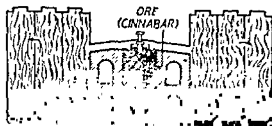


Fig 55·3—Extraction of mercury.

Mercury vaporises and vapours of mercury are condensed in a series of chambers on either side of the furnace as shown.

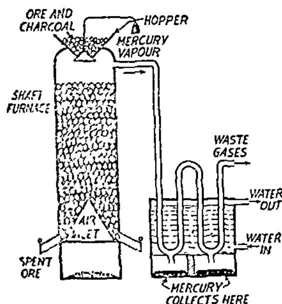
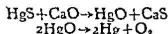


Fig. 55·4—Extraction of mercury using a shaft furnace.

Cinnabar is sometimes mixed with lime or iron oxide before roasting and distillation. The chemical reactions which occur can be represented as follows :


$$HgS + CaO \rightarrow HgO + CaS$$
$$2HgO \rightarrow 2Hg + O_2$$

In modern works ore is heated in a shaft furnace (Fig. 55·4). Lumps of the ore are mixed with fuel (charcoal) and fed into the shaft furnace through a hopper at the top. Fire is started and a current of air is blown in. Cinnabar is reduced to mercury as above and the metal distils over. The vapours are condensed in Y-shaped tubes cooled in water.

(iii) **Purification.** Metal so obtained contains copper, zinc, bismuth and lead as impurities which are removed by filtering through a thick canvas or chamois leather when the suspended impurities are removed. Mercury so filtered is then dropped in a long tube filled with dilute nitric acid (about 5 per cent) as shown in Fig. 55·5. The base metal impurities dissolve in dilute nitric acid as their nitrates. Any mercurous nitrate, if formed, reacts with the impurities forming their nitrates and displacing mercury.

Further purification of mercury, if needed, is carried out by vacuum distillation or fractional electrolysis.

16. Properties of Mercury.

(*a*) **Physical.** (*i*) Mercury is a silver-white shining heavy liquid with a specific gravity of 13·6.

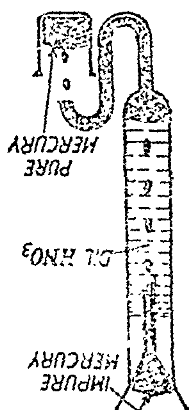


Fig. 55·5—Purification of mercury.

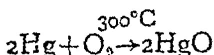
(*ii*) It freezes at −38·87°C and boils at 359·6°C giving mono-atomic vapours which are poisonous in nature.

(*iii*) It is a fair conductor of heat and electricity and has a regular coefficient of expansion.

(*iv*) It forms alloys with metals, *e.g.*, gold, silver, sodium and potassium and the alloys are known as amalgams.

(*b*) **Chemical.** (*i*) Mercury shows a variable valency, positive 1 in mercurous salts and positive 2 in mercuric salts.

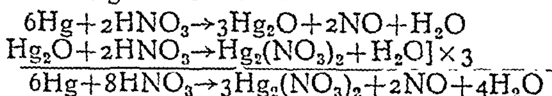
(*ii*) *Action of air.* Mercury tarnishes slowly in air unless heated to about 300°C when it forms mercuric oxide which decomposes to give mercury again at a higher temperature.



$$2Hg + O_2 \xrightarrow{300°C} 2HgO$$

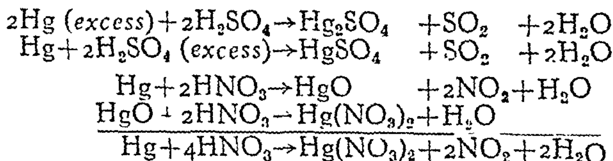
(*iii*) *Action of water and alkalis.* Mercury is not attacked by water or alkalis.

(*iv*) *Action of acids.* Dilute acids have no action on mercury except nitric acid which gives mercurous nitrate and nitric oxide.



$$6Hg + 2HNO_3 \rightarrow 3Hg_2O + 2NO + H_2O$$
$$[Hg_2O + 2HNO_3 \rightarrow Hg_2(NO_3)_2 + H_2O] \times 3$$
$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

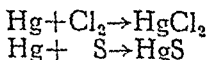
Hot concentrated sulphuric acid gives sulphur dioxide with mercury whereas concentrated nitric acid gives mercuric nitrate and nitrogen dioxide.



$$2Hg\ (excess) + 2H_2SO_4 \rightarrow Hg_2SO_4 + SO_2 + 2H_2O$$
$$Hg + 2H_2SO_4\ (excess) \rightarrow HgSO_4 + SO_2 + 2H_2O$$

$$Hg + 2HNO_3 \rightarrow HgO + 2NO_2 + H_2O$$
$$HgO + 2HNO_3 \rightarrow Hg(NO_3)_2 + H_2O$$
$$Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

(*v*) *Action of halogens and sulphur.* It combines directly with halogens and sulphur.



$$Hg + Cl_2 \rightarrow HgCl_2$$
$$Hg + S \rightarrow HgS$$

(*vi*) All soluble salts of mercury are extremely poisonous in nature.

17. Uses of Mercury.—(*i*) It finds use in thermometers, barometers, manometers and high vacuum air pumps.

(*ii*) It is used in the extraction of gold and silver by the amalgamation process.

(iii) Mercury is used in the preparation of its alloys with ther metals called amalgams. Amalgams of tin, silver and gold re used in dentistry and sodium amalgam is an important reducng agent.

(iv) In Castner-Kellner cell for the manufacture of caustic oda mercury is used as an electrode.

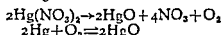
(v) Mercury vapour lamps give a blue light, rich in ultraiolet rays and mercury arc rectifiers are used in charging atteries.

(vi) In the manufacture of its salts and in medicine.

COMPOUNDS OF MERCURY

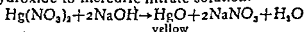
18. **Mercurous Oxide, Hg_2O.**—It is obtained as a brownsh black precipitate when sodium hydroxide is added to a mercurous salt solution. On warming or on exposure to light it readily decomposes into mercury and mercuric oxide. It is regarded a mixture of finely divided mercury and mercuric oxide (HgO.Hg) as indicated by its X-ray diagram.

19. **Mercuric Oxide, HgO.**—It is produced as a red powder by decomposing the nitrate by heat or by heating mercury for a long time in air at 300°C.



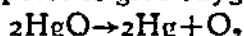
$$2Hg(NO_3)_2 \rightarrow 2HgO + 4NO_2 + O_2$$
$$2Hg + O_2 \rightleftharpoons 2HgO$$

A yellow variety of mercuric oxide is obtained by adding sodium hydroxide to mercuric nitrate solution.



$$Hg(NO_3)_2 + 2NaOH \rightarrow \underset{\text{yellow}}{HgO} + 2NaNO_3 + H_2O$$

On heating, the yellow variety changes to red variety but on strong heating it decomposes to give oxygen.



$$2HgO \rightarrow 2Hg + O_2$$

The difference between the red and yellow varieties is only of the particle size, the particles of yellow variety are smaller. The red variety is used as pigments.

20. **Mercurous Chloride, Calomel, Hg_2Cl_2.**

Preparation. Calomel is prepared—

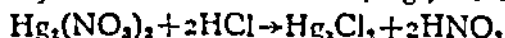
(i) By subliming a mixture of mercuric chloride and metallic mercury.



$$HgCl_2 + Hg \rightleftharpoons Hg_2Cl_2$$

The sublimate is treated with cold dilute nitric acid to remove any metallic mercury and then washed thoroughly to remove any mercuric chloride.

(ii) By adding an excess of hydrochloric acid or any other chloride to any soluble mercurous salt, *e.g.*, mercurous nitrate.



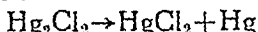
$$Hg_2(NO_3)_2 + 2HCl \rightarrow Hg_2Cl_2 + 2HNO_3$$

Properties. It is a white amorphous substance insoluble in water. Its dissolution in chlorine water or aqua regia is due to the formation of soluble mercuric chloride.



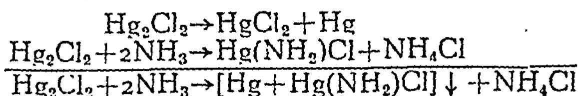
$$Hg_2Cl_2+Cl_2=2HgCl_2$$

On heating strongly it dissociates as follows :



$$Hg_2Cl_2\rightarrow HgCl_2+Hg$$

With ammonia it is turned black due to the formation of finely divided mercury and ammono-basic chloride.

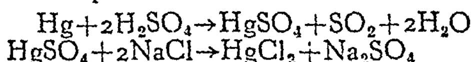


$$\begin{array}{l} Hg_2Cl_2\rightarrow HgCl_2+Hg \\ Hg_2Cl_2+2NH_3\rightarrow Hg(NH_2)Cl+NH_4Cl \\ \hline Hg_2Cl_2+2NH_3\rightarrow[Hg+Hg(NH_2)Cl]\downarrow+NH_4Cl \end{array}$$

Uses. It is used in medicine as purgative.

21. Mercuric Chloride, Corrosive sublimate, $HgCl_2$.

Preparation. Mercuric chloride is prepared these days by heating mercuric sulphate with an equal quantity of sodium chloride in the presence of a little manganese dioxide. Mercuric sulphate needed is obtained by evaporating a solution of mercury in hot concentrated sulphuric acid.



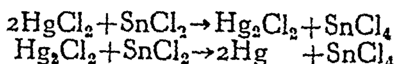
$$Hg+2H_2SO_4\rightarrow HgSO_4+SO_2+2H_2O$$
$$HgSO_4+2NaCl\rightarrow HgCl_2+Na_2SO_4$$

The mixture is heated in a long-neck, flat-bottom flask when mercuric chloride sublimes and collects in the upper cool parts. Manganese dioxide prevents the formation of any mercurous chloride.

Properties. (*i*) It is a colourless, crystalline substance, moderately soluble in cold water, more in hot water.

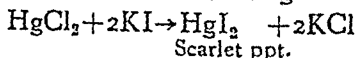
(*ii*) It is a dangerous poison, the antidote being white of an egg which is coagulated by the salt in the system and is eliminated by the system with salt absorbed in it.

(*iii*) *With stannous chloride*, it gives a white precipitate of mercurous chloride (Hg_2Cl_2) which is finally reduced to metallic mercury (grey).

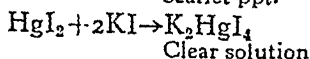


$$2HgCl_2+SnCl_2\rightarrow Hg_2Cl_2+SnCl_4$$
$$Hg_2Cl_2+SnCl_2\rightarrow 2Hg+SnCl_4$$

(*iv*) *With potassium iodide*, it gives a scarlet precipitate soluble in excess of potassium iodide forming Nessler's solution.

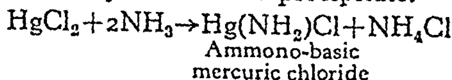


$$HgCl_2+2KI\rightarrow \underset{\text{Scarlet ppt.}}{HgI_2}+2KCl$$



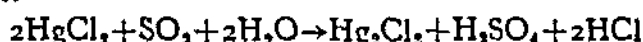
$$HgI_2+2KI\rightarrow \underset{\text{Clear solution}}{K_2HgI_4}$$

(*v*) With ammonia it yields a white precipitate.



$$HgCl_2+2NH_3\rightarrow \underset{\text{Ammono-basic mercuric chloride}}{Hg(NH_2)Cl}+NH_4Cl$$

(*vi*) It is reduced to mercurous chloride by sulphur dioxide and arsenites.



$$2HgCl_2+SO_2+2H_2O \rightarrow Hg_2Cl_2+H_2SO_4+2HCl$$

Uses. (i) Its aqueous solution —mercury lotion—is used as an antiseptic.

(ii) It is employed as wood or skin preservative.

(*iii*) Mercuric chloride also finds use in the preparation of dry cells.

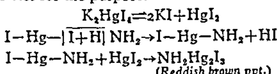
22. **Mercuric Iodide, HgI_2.**—It is obtained as a scarlet precipitate when potassium iodide solution is added to any mercuric salt solution.



$$HgCl_2+2KI \rightarrow \underset{\text{Scarlet ppt.}}{HgI_2} + 2KCl$$

The scarlet precipitate is soluble in excess of potassium iodide due to the formation of a complex compound, potassium-mercuric iodide, $KHgI_3$ or K_2HgI_4. A solution of this compound containing excess of potassium hydroxide is used for detection of ammonium salts under the name *Nessler's reagent.*

23. **Nessler's Reagent.**—Preparation of this reagent is given above. It is used for detecting ammonium salts with which it gives a reddish brown precipitate or yellow coloration. This is a very sensitive test for the purpose.



$$K_2HgI_4 \rightleftharpoons 2KI+HgI_2$$

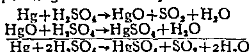
$$I-Hg-|\overline{I+H}|\,NH_2 \rightarrow I-Hg-NH_2+HI$$

$$I-Hg-NH_2+HgI_2 \rightarrow \underset{\text{(Reddish brown ppt.)}}{NH_2Hg_2I_3}$$

Previously the reddish brown ppt. was given the formula $(Hg_2O)NH_2I$.

24. **Mercuric Sulphate, $HgSO_4$.**—It is formed as a white precipitate when sulphuric acid is added to mercurous nitrate solution. It may also be prepared by warming concentrated or fuming sulphuric acid with excess of mercury when a coarse crystalline powder is obtained on cooling. Mercurous sulphate is used as a depolariser in the Weston cell.

25. **Mercuric Sulphate, $HgSO_4$.**—It is prepared by heating mercury with about 1½ times its weight of concentrated sulphuric acid and evaporating the mass to dryness.

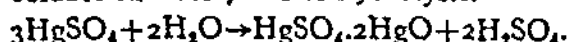


$$Hg+H_2SO_4 \rightarrow HgO+SO_2+H_2O$$

$$HgO+H_2SO_4 \rightarrow HgSO_4+H_2O$$

$$Hg+2H_2SO_4 \rightarrow HgSO_4+SO_2+2H_2O$$

It forms $HgSO_4.H_2O$ crystals with a small quantity of water. In excess of water it gives $HgSO_4.2HgO$, a yellow crystalline powder, sparingly soluble in water, due to hydrolysis.



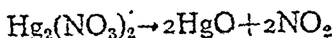
$$3HgSO_4+2H_2O \rightarrow HgSO_4.2HgO+2H_2SO_4.$$

On heating at 400°C mercuric sulphate decomposes to give mercurous sulphate.



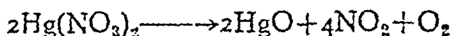
$$3HgSO_4 \rightarrow Hg_2SO_4+Hg+2SO_2+2O_2$$

26. **Mercurous Nitrate, $Hg_2(NO_3)_2.2H_2O$.**—It is prepared by the action of cold dilute nitric acid on mercury (*excess*) when white crystals separate on standing. In contact with water the crystals give a precipitate of the basic nitrate which is soluble in dilute nitric acid. On heating, it decomposes into mercuric oxide and nitrogen dioxide.

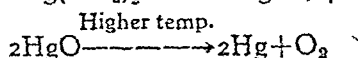


$$Hg_2(NO_3)_2 \rightarrow 2HgO + 2NO_2$$

27. **Mercuric Nitrate, $Hg(NO_3)_2$.**—It is prepared by heating mercury with excess of concentrated nitric acid. It forms colourless deliquescent crystals soluble in water. With water it gives the basic salt, $Hg(NO_3)_2.2HgO$ (white powder). It is precipitated from solution by concentrated nitric acid and decomposes on heating.



$$2Hg(NO_3)_2 \longrightarrow 2HgO + 4NO_2 + O_2$$



$$2HgO \xrightarrow{\text{Higher temp.}} 2Hg + O_2$$

28. **Mercurous Carbonate, Hg_2CO_3.**—It is obtained as a yellow precipitate when potassium bicarbonate solution is added to mercurous nitrate solution. It decomposes on gentle heating (130°C) or on exposure to light.



$$Hg_2CO_3 \rightarrow HgO + Hg + CO_2$$

29. **Mercuric Carbonate.**—It is known only in the form of basic carbonates, $HgCO_3.2HgO$ (yellow) and $HgCO_3.3HgO$ (brown). These are obtained as precipitates by treating mercuric nitrate solution with a large excess of potassium carbonate and potassium bicarbonate solution respectively.

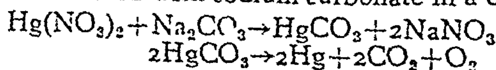
30. **Mercuric Sulphide, HgS.**—It occurs native as cinnabar and may be obtained as black precipitate, by passing hydrogen sulphide through mercuric chloride or by rubbing mercury and sulphur mixture with potassium hydroxide when the black sulphide first formed changes to crystalline red variety.

It is insoluble in hot dilute nitric acid and in yellow ammonium sulphide. It dissolves in aqua regia due to the formation of mercuric chloride. The black variety on sublimation changes red and is used as a pigment, and in Ayurvedic medicines (*Makaradhwaja Rasasindur*).

31. **Mercuric Thiocyanate, $Hg(CNS)_2$.**—It is obtained as a white precipitate by adding potassium thiocyanate, KCNS to mercuric nitrate solution. When made into a small tablet with gum and lit, it gives a long snake-like mass (*Pharaoh's serpent*).

32. **Tests for Mercury.**—(*i*) Most of the mercury salts sublime on heating.

(*ii*) All mercury salts give a sublimate of metallic mercury (grey mirror) when heated with sodium carbonate in a dry test tube.



$$Hg(NO_3)_2 + Na_2CO_3 \rightarrow HgCO_3 + 2NaNO_3$$
$$2HgCO_3 \rightarrow 2Hg + 2CO_2 + O_2$$

(*iii*) Copper chips when placed in a mercury salt solution, get coated with a layer of mercury.

33. Distinction between Mercurous and Mercuric Salts.—The following wet tests are performed to distinguish between mercurous and mercuric salts.

Tests	Mercurous salts	Mercuric salts
1. Dilute hydrochloric acid.	White ppt. of Hg_2Cl_2, insoluble in hot water and aqua regia and is blackened by ammonia.	No ppt.
2. Salt soln. $+H_2S$.	Immediate black ppt. of HgS and mercury. $Hg_2(NO_3)_2+H_2S \rightarrow HgS+Hg+2HNO_3$	A ppt. changing colour from white to yellow, brown and finally black (HgS formed).
3. Sodium hydroxide.	Black ppt. of Hg_2O insoluble in excess of NaOH.	Reddish-brown ppt. of basic chloride first formed changes yellow with excess of NaOH forming HgO.
4. Ammonium hydroxide.	Give black ppt. of ammono basic mercuric salt and finely divided mercury	Give white ppt. of ammono basic mercuric chloride. $(NH_2)HgCl$.
5. Stannous chloride.	White ppt. of Hg_2Cl_2 changing grey black with excess of $SnCl_2$	The same.
6. Potassium iodide.	Yellowish green ppt. of Hg_2I_2, changing grey with excess due to metallic mercury.	Scarlet ppt. soluble in excess due to the formation of $KHgI_3$ or K_2HgI_4

TEST YOURSELF ON THESE REACTIONS

Write equations for the chemical reactions, if any, between :

1. Action of heat on : (i) Zinc blende ; (ii) Zinc sulphate ; (iii) Zinc carbonate ; (iv) Zinc ; (v) Cinnabar alone or mixed with lime , (vi) Mercury ; (vii) Mercurous carbonate.

2. Zinc+ (i) Boiling water , (ii) Dilute and concentrated sulphuric acid ; (iii) Nitric acid ; (iv) Caustic soda ; (v) Sulphur ; (vi) Chlorine ; (vii) Mercuric chloride.

3. Zinc sulphate+(i) Barium sulphide , (ii) Sodium bicarbonate ; (iii) Sodium hydroxide , (iv) Potassium ferrocyanide

4. Mercury+(i) Nitric acid (Dil. and conc) , (ii) Conc. sulphuric acid ; (iii) Chlorine , (iv) Sulphur , (v) Mercuric chloride (sublimed).

5. Mercurous chloride+(i) Ammonia , (ii) *Heated* ; (iii) *Chlorine* water or aqua regia.

6. Mercuric sulphate+sodium chloride.

7. Mercuric chloride+(i) Stannous chloride , (ii) Potassium iodide ; (iii) Ammonia.

QUESTIONS

1 How does zinc occur in nature and how is this metal extracted in a pure state ? Explain its reactions with (a) atmospheric air , (b) dilute and concentrated nitric and sulphuric acids ; and (c) copper sulphate solution.
(Delhi H S 1971, 70, 68, 65)

2. Outline the important steps in the manufacture of pure zinc from zinc blende. *(All India H.S. 1970)*

3. How are magnesium and zinc obtained ? Describe in detail the properties of these metals and their compounds and hence justify the inclusion of these metals in one group. *(Delhi Pre-Univ. 1969)*

4. (*a*) What are the important ores of mercury ? How is the metal extracted from these ores and purified ? How are its chlorides obtained ?
(Delhi H.S. 1969, 68, 64 ; Punjab H.S. 1962)

(*b*) What is the action of solution of (i) Potassium iodide, (ii) Stannous chloride, (*iii*) Sodium hydroxide, and (*iv*) Ammonia on a solution of mercuric chloride ?

(*c*) What happens when mercury is treated with (*i*) ozone, (*ii*) nitric acid, and (*iii*) sulphuric acid ? By what methods can mercuric chloride be converted into mercurous chloride and *vice versa*. *(Delhi H.S. 1964)*

5. Give the preparation, properties and uses of any two of the following compounds :

(*i*) Zinc chloride.

(*ii*) Zinc oxide.

(*iii*) Corrosive sublimate.
(Delhi H.S. 1968 ; Punjab H.S. 1963 ; Pre-Univ. 1963, 62 ; Inter. 1960)

(*iv*) Calomel. *(Delhi Prep. 1960 ; Pre-Medical 1963, 61 ; Punjab 1960)*

(*v*) Lithopone.

(*vi*) Magnesium sulphate. *(Punjab H.S. 1963, 62)*

(*vii*) Zinc sulphide. *(Delhi H.S. 1963)*

6. How would you detect (*a*) Mercuric salt in a sample of calomel and (*b*) mercurous salt in a sample of mercuric nitrate ? Give equations ?

7. Give all tests you would perform to distinguish between a mercurous salt and a mercuric salt.

8. Write a short note on Galvanizing. *(Punjab H.S. 1962)*

A KEY METAL OF MODERN LIFE - ALUMINIUM

NOT SO MANY YEARS AGO	TODAY
PURE ALUMINIUM WAS A CHEMICAL CURIOSITY Rs. 1500/- PER kg.	HUNDREDS OF THOUSANDS TONS OF ALUMINIUM PRODUCED ANNUALLY ABOUT Rs.5/- PER kg

56

IA	IIA	IIIA	IVA	VA	VIA	VIIA
Li	Be	B	C	N	O	F
Na	Mg		Si	P	S	Cl

Aluminium

1. General.—Aluminium is placed in Group IIIA of the Periodic Table along with boron, gallium, indium and thallium. General characteristics of this group are :

(i) With the exception of boron and aluminium, the elements of Group IIIA are all rare.

(ii) They all contain 3 electrons in their outermost orbit (as given in the table below) and are, therefore, trivalent.

Element	At. Wt.	At. No.	Electronic arrangement	M.P.	B.P.	Colour of solid
Boron	10·82	5	2, 3	2300	2500	Transparent crystals
Aluminium	26·97	13	2, 8, 3	658·7	1800	Silver-white
Gallium	69·72	31	2, 8, 18, 3	29·78	2000	Silver-white
Indium	114·76	49	2, 8, 18, 18, 3	155	1450	Silver-white
Thallium	204·30	81	2, 8, 18, 32, 18, 3	302	1457	Silver-white

(iii) Metallic character goes on increasing. Boron is a non-metal, aluminium is an amphoteric element and the rest are metals.

Hydroxide of boron is acidic, the amphoerict aluminium hydroxide is slightly more basic than acid whereas the hydroxides of remaining elements are basic.



Charles Martin-Hall
(1863-1914)

American chemist who discovered the modern method of extraction of aluminium by electrolysis of bauxite in 1886.

Boron resembles silicon more than aluminium (*see* page 2·259).

2. **Historical.**—Aluminium was discovered in 1825 by Oersted. Wohler isolated the metal in 1827 by the action of potassium on aluminium chloride. The present electrolytic method for the extraction of aluminium by electrolysis of alumina in fused cryolite was discovered simultaneously by Charles M. Hall in America and Heroult in France in 1886.

3. **Occurrence.**—Aluminium does not occur free in nature. In the combined state it is the third most abundant element found in nature and forms 7·28 per cent of the earth's crust. It occurs as :

(*i*) *Oxides, e.g.*, corundum, Al_2O_3 ; diaspore, $Al_2O_3.H_2O$ and bauxite, $Al_2O_3.2H_2O$. Bauxite is the chief ore of aluminium and is found in Kashmir, Bihar, Orissa, Saurashtra, Kutch, Madhya Pradesh and Tamil Nadu.

(*ii*) *Fluoride, e.g.*, cryolite, Na_3AlF_6.

(*iii*) *Silicates, e.g.*, rocks like *felspar*, $KAlSi_3O_8$; mica and tourmaline clays, *e.g.*, kaolin and slate, are also silicates of aluminium.

(*iv*) *Basic sulphates, e.g.*, Alunite or alumstone, $K_2SO_4.Al_2(SO_4)_3$. $4Al(OH)_3$.

In India there are two companies producing aluminium—the Indian Aluminium Company, Alwaye (Kerala), and Aluminium Corporation of India Ltd., Jaykaynagar (West Bengal). During the current Five-Year Plan these companies will expand and three new plants are proposed to be set up. One of them will be located at Salem (Tamil Nadu), second at Rihand (U.P.) and third at Koyna.

Main technical problems facing aluminium industry in India are :

(*a*) Indian bauxite is refractory in nature and more expensive to treat than some of the deposits obtained by other countries.

(*b*) Adequate supply of cheap electric power is lacking as yet. With the availability of more hydro-electric power this difficulty will be solved.

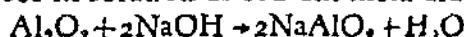
Estimates of Total Capacity and Production of Aluminium in India
(in thous[illegible] tonnes)

	1960-61	1965-66	1970-71	1975-76
Capacity				
Ingots	19	69	280	400
Sheets	22·8	100	190	300
Production				
Ingots	19	68	250	360
Sheets	26·8	10[illegible]	190	300

Ext[illegible] ually isolated from bauxite [illegible] difficult to purify alumi- [illegible] during electrolysis. The [illegible] step in the extraction of aluminium is, therefore, the purification of bauxite. This is followed by electrolysis and then purification of impure aluminium is as described below :

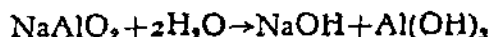
(1) **Purification of Bauxite.** The method used depends upon the nature of the impurity present. "Red bauxite" containing iron as impurity is purified by Baeyer's process or Hall's process.

(*a*) **Baeyer's Process.** Finely ground ore is roasted to convert ferrous oxide to ferric oxide and then digested at 150°C with concentrated caustic soda solution for a few hours in an autoclave when alumina goes in solution as sodium meta-aluminate, $NaAlO_2$.



$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

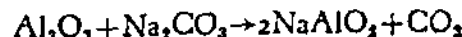
Ferric oxide left undissolved is filtered off. The filtrate is diluted largely, inoculated with aluminium hydroxide precipitate and churned when sodium meta-aluminate hydrolyses to aluminium hydroxide.



$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$$

Precipitated aluminium hydroxide is ignited to get alumina, Al_2O_3.

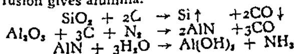
(*b*) **Hall's Process.** Here the ore is fused with sodium carbonate when soluble sodium meta-aluminate, $NaAlO_2$ is produced. This is extracted with water when iron oxide is left behind in the residue.



$$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2$$

The water extract is heated to 50—60°C and carbon dioxide is passed through [illegible] due [illegible]

(*c*) **Serpek's Process.** The powdered bauxite is mixed with coke and heated to 1800°C in a current of nitrogen. Silica present is reduced to silicon which volatilizes off and alumina gives aluminium nitride. This can be hydrolysed to aluminium hydroxide which on fusion gives alumina.



$$SiO_2 + 2C \rightarrow Si\uparrow + 2CO\uparrow$$
$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO$$
$$AlN + 3H_2O \rightarrow Al(OH)_3 + NH_3$$

(2) Electrolysis of fused alumina. Pure alumina is then dissolved in fused cryolite, Na_3AlF_6 *and electrolysed in* an iron tank, *T*, lined with gas carbon, *C.L.* (Fig. 56·1).

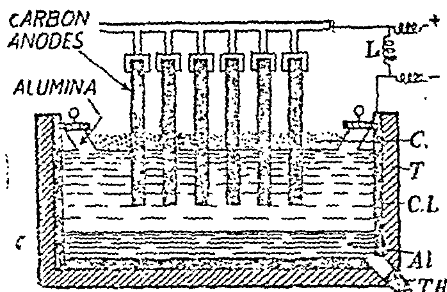


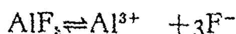
Fig. 56·1—Electrolysis of fused alumina.

The carbon lining serves as the cathode while a number of carbon rods dipping in the fused mass serve as the anode. Heat produced by the current keeps the mass in fused state at 900—950°C.

As a result of decomposition of alumina by electric current (100 amperes at 6-7 volts), aluminium is produced and sinks to the bottom while oxygen appears at the anodes which are oxidized thereby and have to be replaced from time to time. As concentration of alumina falls below a certain minimum, the resistance of the bath increases and is indicated by the charge control lamp which glows. More alumina is added to make up for the loss. Aluminium metal is tapped from time to time through the tapping hole. *T.H.* near the bottom. The metal obtained is about 99 per cent pure.

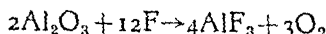
The exact nature of the action which takes place is not certain. It is probably as follows :

Aluminium fluoride (from cryolite) ionizes :



$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

Al^{3+} ions move to cathode and are discharged there as aluminium metal. F^- ions are discharged as fluorine at the anode. Here they react with alumina reforming aluminium fluoride and oxygen.



$$2Al_2O_3 + 12F \rightarrow 4AlF_3 + 3O_2$$

Oxygen evolved at the anode either escapes as a gas or unites with carbon of the anodes to give carbon monoxide which either burns or escapes. Thus it is only the dissolved alumina that is decomposed and has to be added from time to time. Some aluminium fluoride is, however, always lost by vaporization. The layer of powdered coke, *C* kept on the surface of the molten liquid serves to prevent heat losses by radiation and keeps down the loss of aluminium fluoride. This layer of coke also prevents the burning of carbon electrodes in the air at the point where these emerge from the bath.

(3) Refining of Aluminium. Although *purification of aluminium* has not been found economical in the past, large quantities of the metal are being refined today by the Hoopes' electrolytic

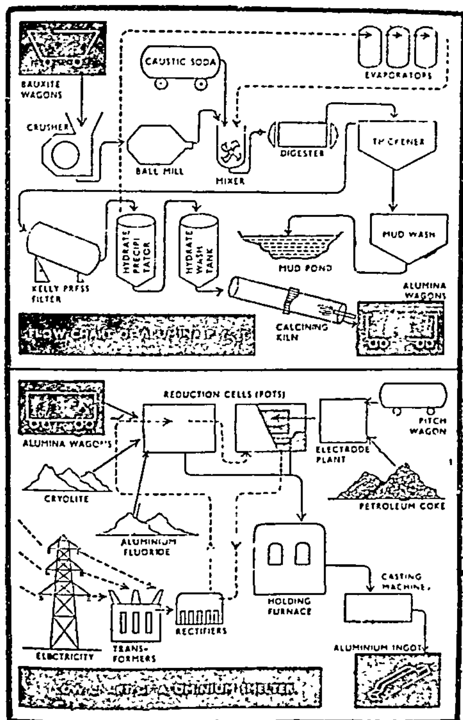


Fig. 56.2—Manufacture of Aluminium from Bauxite by Indian Aluminium Company, Alwaye (Kerala), with its smelters at Hirakud and Alupuram (Kerala)

process. In a carbon-lined iron tank (Fig. 56·3) are placed three layers differing in specific gravity. Molten impure aluminium containing copper and silicon (to increase its density) forms the bottom layer and serves as the anode. A mixture of fluorides of sodium, barium, aluminium, in the fused state and saturated with alumina constitutes the middle layer. Pure molten aluminium is the top layer serving as cathode.

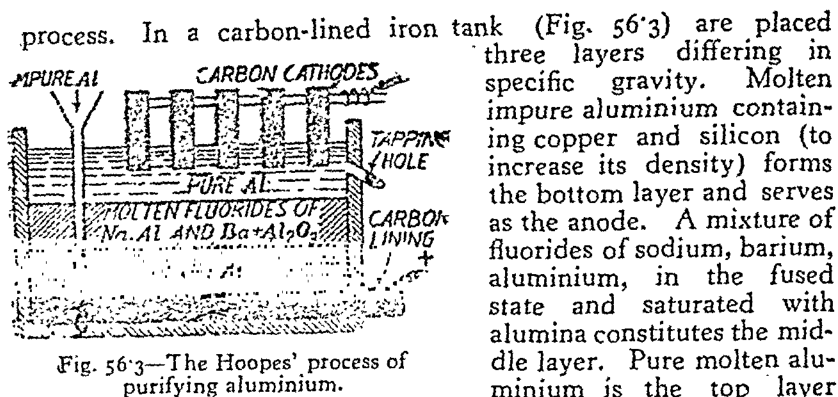


Fig. 56·3—The Hoopes' process of purifying aluminium.

On passing electric current aluminium from the middle layer passes into the upper layer and an equivalent amount from the base layer passes into the middle layer. Pure aluminium is tapped from the top. It is 99·98 per cent pure.

5. **Properties of Aluminium.**

(*a*) **Physical.** (*i*) Aluminium is a bluish white and extremely light metal with specific gravity=2·7.

(ii) It stands second in malleability and sixth in ductility among the metals but is not so tenacious as brass, copper or steel.

(*iii*) It ranks with the best conductors of electricity. In conductivity it is excelled only by silver, copper and gold. Weight for weight, it is twice as good a conductor as copper.

(*iv*) It can be easily welded or cast but can be soldered using a special solder only with difficulty.

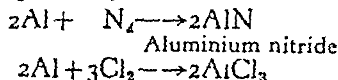
(*b*) **Chemical.** (*i*) It is a trivalent electropositive metal.

(*ii*) *Action of air.* It takes a high polish but is soon coated with a thin protective layer of aluminium oxide. It is thus a self-protective metal. If heated to redness, it burns with a brilliant white light with the evolution of much heat.



$$4Al + 3O_2 \rightarrow 2Al_2O_3 + 772{,}000 \text{ cal.}$$

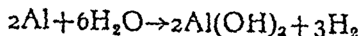
(*iii*) *Combination with nitrogen and halogens.* It directly combines on heating with nitrogen and halogens forming nitride and the halides respectively.



$$2Al + N_2 \longrightarrow \underset{\text{Aluminium nitride}}{2AlN}$$

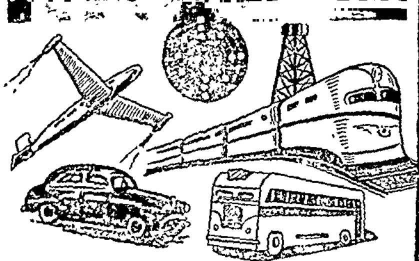
$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

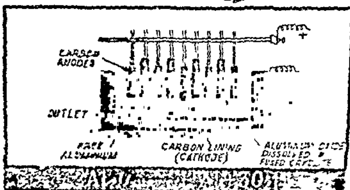
(*iv*) *Action of water.* Pure water has almost no action on aluminium in cold. Salt water (*e.g.*, sea water) corrodes it rapidly especially when it is hot. It decomposes boiling water liberating hydrogen.

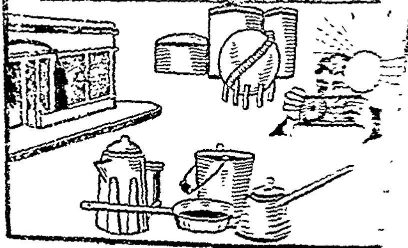


$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2$$

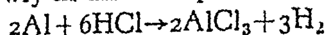
ALUMINUM AND ITS USES





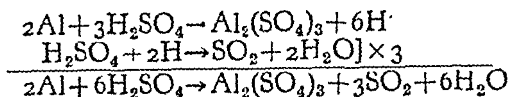


(*v*) *Action of acids*. Aluminium dissolves readily in hydrochloric acid and slowly in dilute sulphuric acid liberating hydrogen.



$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

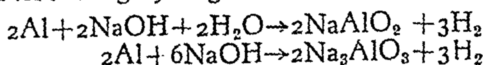
Hot concentrated sulphuric acid gives sulphur dioxide with aluminium.



$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H$$
$$[H_2SO_4 + 2H \rightarrow SO_2 + 2H_2O] \times 3$$
$$2Al + 6H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

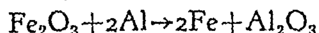
Nitric acid whether dilute or concentrated hardly affects aluminium at all.

(*vi*) *Action of alkalis*. Strong bases like sodium or potassium hydroxide react with the metal forming meta-aluminates or aluminates and liberating hydrogen.



$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$
$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2$$

(*vii*) *Reducing action*. The metal reduces many other metallic oxides (*Aluminothermic process, see below*).



$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

6. Uses.—(*i*) Being light and good conductor of electricity, aluminium is used to some extent in place of copper, for making electrical transmission cables.

(*ii*) Aluminium powder is used in silver paints (mixture with linseed oil), in thermit welding and extraction of chromium and manganese.

(*iii*) As a deoxidiser used for removing blow holes, in metallurgy.

(*iv*) In making utensils and various novelty articles.

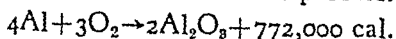
(*v*) For making alloys used in aircraft, automobiles and speed boats.

(*vi*) As foil in wrapping cigarettes and confectionery.

(*vii*) A mixture of aluminium powder and aluminium nitrate, *ammonal* is used in bombs.

(*viii*) Aluminium powder is used in flashlight bulbs for indoor photography.

7. **Thermit Welding.**—Aluminium has got a great affinity for oxygen and its oxidation is an exothermic process.



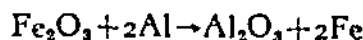
$$4Al + 3O_2 \rightarrow 2Al_2O_3 + 772{,}000 \text{ cal.}$$

The enormous amount of heat produced is used in welding rails or heavy parts of machinery without removing them from their position. This is called thermit welding or Goldschmidt's Aluminothermic process after the name of its discoverer, Goldschmidt, a German chemist.

A mixture of ferric oxide (3 parts) and aluminium powder (1 part) called *thermit* is placed in a funnel-shaped crucible (Fig. 56·5) lined inside with magnesite. This is covered with a mixture of aluminium powder and barium peroxide called *ignition mixture* in which a fuse of magnesium ribbon is inserted.

The broken ends, say of a girder, are brought near each other and surrounded by a fire-clay mould with a hole at the top.

When the magnesium ribbon fuse is lighted, the ignition mixture catches fire and reduction of iron oxide by aluminium powder occurs.



$$Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe$$

The reaction occurs at a high temperature but once started proceeds very rapidly and vigorously. So much heat is produced

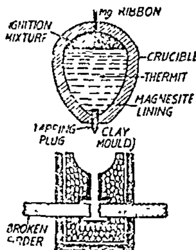


Fig. 56·5—Thermit welding of two broken parts of a girder.



Goldschmidt Hans (1861—1923)
German chemist, he invented the alumino-thermic or thermit process named after him

that iron melts. Molten iron is allowed to flow through the tapping plug into the clay mould. The broken ends of rails which are pre-heated, melt on coming into contact with molten iron. Thus on solidification the two broken pieces become one single piece. The superfluous metal, sticking to it, is trimmed off.

8. **Alloys of Aluminium.**

(i) *Magnalium.* (*See* page 2·337).

(ii) *Aluminium bronze.* (*See* page 2·322).

(iii) *Duralumin.* It contains about 95% aluminium, 4% copper, 0·5% manganese and 0·5% magnesium. It compares steel in strength though half as dense as steel. It is used for making aeroplane parts.

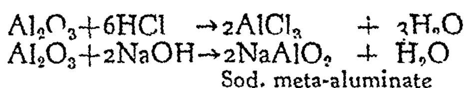
-luminium, 5% copper,
e worked both hot and

COMPOUNDS OF ALUMINIUM

9. **Aluminium oxide, Alumina, Al_2O_3.**—*Bauxite* is a hydrated oxide of aluminium. *Corundum* and *emery* are also the oxides of the metal and occur in nature. These are used as abrasives.

Rubies and sapphires are pure specimens of the oxide and are used as precious stones. Their colours are due to traces of metallic oxides. These are being prepared synthetically by fusing pure alumina in oxy-hydrogen blow-pipe flame.

It is an amphoteric oxide and dissolves both in acids as well as alkalis.



$$Al_2O_3+6HCl \rightarrow 2AlCl_3 + 3H_2O$$
$$Al_2O_3+2NaOH \rightarrow \underset{\text{Sod. meta-aluminate}}{2NaAlO_2} + H_2O$$

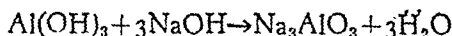
Alumina is used as a refractory material for lining furnaces. *Alundum*, obtained by fusing bauxite, is used as an abrasive. Bauxite is used for extraction of aluminium and in the manufacture of aluminium salts.

10. **Aluminium Hydroxide, $Al(OH)_3$.**—If we add a little ammonium hydroxide to a solution of an aluminium salt, say aluminium chloride, a white gelatinous precipitate of aluminium hydroxide is obtained.



$$AlCl_3+3NH_4OH \rightarrow Al(OH)_3\downarrow +3NH_4Cl$$

The precipitate dissolves in excess of a caustic alkali giving aluminates.



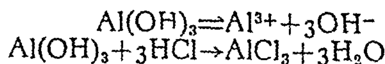
$$Al(OH)_3+3NaOH \rightarrow Na_3AlO_3+3H_2O$$

In presence of an alkali, it behaves as an acid and ionizes as follows :



$$Al(OH)_3 \rightleftharpoons 3H^+ + AlO_3^{3-}$$

With acids, it acts as a weak base and ionizes to a slight degree as under :



$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$$
$$Al(OH)_3+3HCl \rightarrow AlCl_3+3H_2O$$

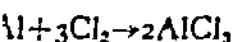
It is used as a mordant in dyeing. Aluminium hydroxide is deposited on a fibre before it is soaked in the solution of a dye. The precipitate within the fibre absorbs the colouring matter to form a '*lake*'.

11. **Aluminium chloride, $AlCl_3$.**—Aluminium chloride is prepared by dissolving aluminium, its oxide or hydroxide in hydrochloric acid. On crystallizing, the hydrated crystals, $AlCl_3.6H_2O$ are obtained. On heating, the crystals decompose as follows :

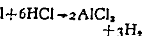


$$2AlCl_3.6H_2O \rightarrow Al_2O_3+6HCl+3H_2O$$

Anhydrous salt cannot, therefore, be prepared by heating the ystals. It is obtained by passing dry chlorine or hydrochloric id gas over heated uminium powder ig. 56·6) when hydrous aluminium loride vapours are otained and condensed in the receiver.



$Al+3Cl_2 \rightarrow 2AlCl_3$



$l+6HCl \rightarrow 2AlCl_3 + 3H_2$

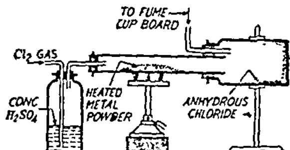


Fig 56 6—Preparation of anhydrous aluminium chloride.

The anhydrous salt may also be prepared by heating a ixture of alumina and coke in a current of chlorine (MacAffe ocess).



$$Al_2O_3+3C+3Cl_2 \rightarrow 2AlCl_3+3CO$$

It is a white crystalline and deliquescent substance which mes in air. On heating it sublimes at 185°C and its vapour nsity corresponds to the formula Al_2Cl_6 below 350°C whereas ove 750°C as well as in solution its molecular weight corresponds the formula $AlCl_3$. An aqueous solution of the salt is acidic in ture due to hydrolysis.



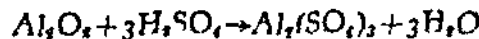
$$AlCl_3+3H_2O \rightleftharpoons Al(OH)_3+3HCl$$

With ammonia, it forms an addition compound, $AlCl_3.6NH_3$.

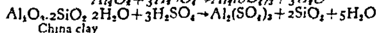
Uses. (i) It is employed as a catalyst in Friedel-Crafts reaction and in the manufacture of gasoline by cracking of high iling fractions of petroleum.

(ii) It is also used in the manufacture of dyes, drugs and rfumes.

12. Aluminium sulphate, $Al_2(SO_4)_3$ —It is prepared on a mmercial scale by dissolving bauxite or china clay (Kaolin) in lphuric acid.



$$Al_2O_3+3H_2SO_4 \rightarrow Al_2(SO_4)_3+3H_2O$$



$$\underset{\text{China clay}}{Al_2O_3.2SiO_2\,2H_2O}+3H_2SO_4 \rightarrow Al_2(SO_4)_3+2SiO_2+5H_2O$$

The insoluble residue (sand etc) is filtered off and the filtrate owed to cool when $Al_2(SO_4)_3.18H_2O$ crystals separate.

It is a white crystalline substance. Its solution in water is dic in nature due to hydrolysis. With sulphates of alkali metals, gives double salts called alums.

Uses. Aluminium sulphate is used .

(i) In foamite fire-extinguishers (*see* page 2·241).

(ii) As a mordant in dyeing and in calico-printing.

(iii) In tanning and in purifying water due to its wonderful capacity for coagulating colloidal solutions.

(iv) In the sizing of paper.

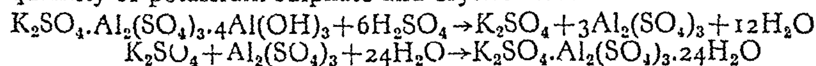
(v) In the manufacture of alums.

13. **The Alums.**—When a mixture of potassium sulphate and aluminium sulphate is dissolved in water and concentrated, a double salt separates in the form of crystals. The composition of the double salt corresponds to the formula $K_2SO_4.Al_2(SO_4)_3.24H_2O$. All double sulphates with similar composition and properties are called *alums*.

Instead of potassium sulphate, sulphate of ammonium or sodium (monovalent radicals) may be used. Similarly aluminium sulphate may be replaced by sulphates of trivalent metals as chromium and iron. Writing X and Y for monovalent and trivalent metals, respectively, the alum may be represented by the general formula, $X_2SO_4.Y_2(SO_4)_3.24H_2O$. These are isomorphous substances, soluble in water.

Common alum (फिटकरी) is *potash alum*, $K_2SO_4.Al_2(SO_4)_3.24H_2O$ and is prepared—

(i) *From alunite or alum stone.* Alunite is boiled with dilute sulphuric acid and filtered. The filtrate is mixed with a requisite quantity of potassium sulphate and crystallized.



$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3+6H_2SO_4 \rightarrow K_2SO_4+3Al_2(SO_4)_3+12H_2O$$
$$K_2SO_4+Al_2(SO_4)_3+24H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$$

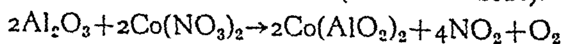
(ii) *From alum shale.* Alum shale is an aluminium silicate containing iron pyrites. It is roasted when aluminium sulphate is formed. This is extracted with water, mixed with potassium sulphate and crystallized.

(iii) *From bauxite.* Bauxite is dissolved in sulphuric acid, treated with calculated amount of potassium sulphate and crystallized.

It is a white crystalline substance soluble in water. On heating it loses its water of crystallization and swells up.

Uses. Alum is used in purification of water, as a mordant in dyeing, for tanning of leather, for sizing of paper and as a styptic to arrest bleeding.

14. **Tests for Aluminium.**—(i) *Charcoal cavity test.* On heating with sodium carbonate in charcoal cavity, aluminium salts give a white infusible residue which glows when hot. On moistening the same with a drop of cobalt nitrate, it changes blue due to the formation of cobalt meta-aluminate (Thenard's blue).



$$2Al_2O_3+2Co(NO_3)_2 \rightarrow 2Co(AlO_2)_2+4NO_2+O_2$$

(ii) *Ammonium hydroxide solution* gives a white gelatinous precipitate of aluminium hydroxide slightly soluble in excess of the reagent. The solubility is decreased by the presence of ammonium chloride due to the common ion effect.

(iii) *Sodium hydroxide solution* gives a white gelatinous precipitate of aluminium hydroxide soluble in excess due to the formation of sodium meta-aluminate.

$$\underset{\text{Gelatinous ppt.}}{Al(OH)_3} + NaOH \rightarrow \underset{\text{Soluble}}{NaAlO_2} + 2H_2O$$

(iv) *Lake test.* A few drops of litmus and ammonium hydroxide in excess are added to the aluminium salt solution in dilute acid. A blue gelatinous precipitate floating in somewhat colourless background is obtained.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Alumina+(i) Sodium hydroxide *(digested)* : (ii) Sodium carbonate *(fused)* : (iii) Hydrochloric acid : (iv) Coke *(heated in a current of chlorine)*; (v) Sulphuric acid (vi) Cobalt nitrate *(fused)*.

2. Sodium meta-aluminate+(i) Water (churned) : (ii) Water+CO_2

3. Bauxite containing sand+coke *(heated in a current of nitrogen)*.

4. Aluminium+(i) air *(heated)* ; (ii) Nitrogen ; (iii) Chlorine ; (iv) Boiling water ; (v) Hydrochloric acid ; (vi) Sulphuric acid ; (vii) Sodium hydroxide ; (viii) Ferric oxide *(heated)*

5. Aluminium chloride+(i) Water , (ii) Ammonium hydroxide.

QUESTIONS

Essay-type Questions

1. How does aluminium occur in nature and how is it extracted ? Describe its important properties and uses (*Delhi H S 1972, 71, 66, 63 ; Delhi Pre-Med 1961 ; Punjab H S 1961 ; Inter. 1961*)

2. What are the ores of aluminium ? What are its uses ? Mention one of its alloys, state its composition and its special quality

3. Describe how aluminium is prepared from alumina Give equations and explain how aluminium reacts with strong sulphuric acid and hot caustic soda. (*All India H S. 1969*)

4. What are alums ? Describe the preparation, properties and uses of potash alum. (*Delhi H S. 1971*)

5. Write a short note on Goldschmidt's Aluminothermic process. (*Punjab Inter 1962 , Kashmir 1960 ; All India H S. 1967*)

Test your Understanding

6. Fill in the blanks in the following

(i) Common ore of aluminium is represented by the formula, .. .

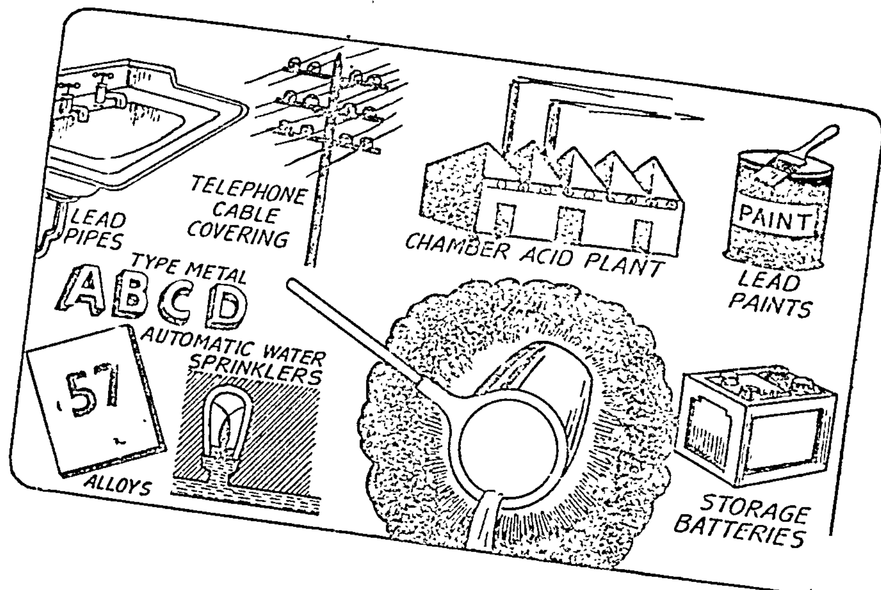
(ii) Red bauxite is purified by heating it with coke in a current of ......This is termed

(iii) Aluminium is extracted by electrolysis of alumina in fused .

(iv) Anhydrous aluminium chloride is obtained by heating . . in a current of . or

KEY

(i) Bauxite, $Al_2O_3.2H_2O$; (ii) Nitrogen, Serpek's process ; (iii) Cryolite ; (iv) *Aluminium powder, dry chlorine*, hydrochloric acid gas.



Lead

1. **Historical.**—Lead is one of the metals known to the ancients. The Romans used it for making water pipes and some lead compounds were employed as cosmetics and paints. The modern symbol, Pb, is derived from its Latin name *Plumbum.*

2. **Occurrence.**—Although lead occurs in nature as the carbonate, *cerrusite*, $PbCO_3$, and the sulphate, *anglesite*, $PbSO_4$, the principal ore of lead is *galena*, PbS, which occurs as greyish-black cubical crystals. The chief lead producing countries are the United States, Spain and Mexico. Lead deposits, now being exploited in India by the Metal Corporation of India, arê located in Udaipur and Jaipur in Rajasthan.

Estimates of Total Capacity and Production of Lead (*in thousand tonnes*) in India.

	1960-61	1965-66	1970-71	1975-76
Capacity	6·1	0·2	25	50
Production	3·8	9·2	25	50

3. **Extraction.**—The method of extraction from its chief ore ends upon the quality of the ore. The richer ore is treated by -reduction Process while the poorer ores are treated by *melting blast furnace* (*Carbon Reduction Process*).

(*a*) **Self-reduction Process for Richer Ores.** The various involved are :

(1) **Crushing and Concentration.** The ore is crushed, powdered and sieved. It is then concentrated by froth on process (*see* page 2·287).

(*ii*) **Roasting.** The concentrated ore is roasted at moderate temperature in excess of air, on the hearth of a reverberatory furnace (Fig. 57·1). It is a special type of furnace provided with doors D_1, D_2 and D_3 which can be opened or closed at will. Galena is oxidised partly to oxide and partly to sulphate.

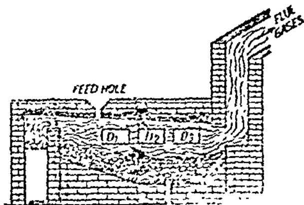
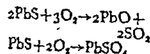
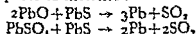


Fig. 57·1 - Reverberatory furnace for extraction of lead.



$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2O_2 \rightarrow PbSO_4$$

(*iii*) **Reduction with more galena.** At this stage the doors are closed and the supply of air is cut off. Now more galena is added and temperature raised when galena reduces both lead oxide and lead sulphate to metallic lead.



$$2PbO + PbS \rightarrow 3Pb + SO_2$$
$$PbSO_4 + PbS \rightarrow 2Pb + 2SO_2$$

Molten lead is drawn off from time to time from the bottom of the furnace.

(*b*) **Carbon-reduction Process for Poorer Ores.** The different steps involved in this process are :

(i) **Crushing and Concentration.** (*As above.*)

(ii) **Roasting and Sinteri**... with lime and roasted in a sinter... mpe- ... mass. ... hood at the top and a grating near the bottom and is mounted on trunnions for charging and discharging (Fig. 57·2). A coal-fire is made on the grating and a charge of ore and lime placed over it. A blast of air is now blown through the grating while the flames produced are sucked away by applying suction from the top of hood. In this way a current of air circulates through the hot charge. Lead sulphide is oxidised to lead oxide, PbO.

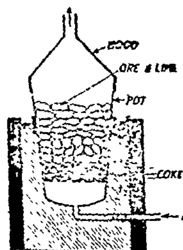


Fig 57·2—Sinterer for roasting of concentrated ore.



$$2PbS + 3O_2 = 2PbO + ...$$

Lime acts as a ... combines with sulphur ... ing the forward ...

As a result of sintering the ore particles become sticky and agglomerate into a compact porous mass.

In a modern method, roasting and sintering are carried out in a sintering machine of the Dwight-Lloyd type (Fig. 57·3). It consists

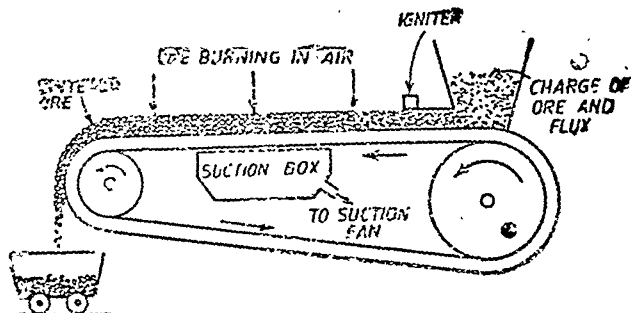


Fig. 57·3—A sintering machine of the Dwight-Lloyd type.

of an endless steel belt moving on rollers. Concentrated and dried ore is mixed with a little coke and lime (*flux*) and mixture dropped slowly over the belt. The belt carrying the ore moves on slowly and passes under a fire box where the ore gets ignited. Burning ore is subjected to a downward draught of air with the help of a suction box under the belt. It continues burning and moving till it topples over, when the belt becomes vertical while turning over the roller.

(*iii*) Smelting. The sintered ore is mixed with coke (*fuel*), lime (*flux*) and smelted in a small blast furnace. It is a tower-like structure made of sheet steel and lined inside with fire-bricks lining (Fig. 57·4). It is about 6 m. high and about 1 m. in width, with its lower part water jacketed. A blast of air necessary for combustion of coke and ore itself is blown through the air blast main below.

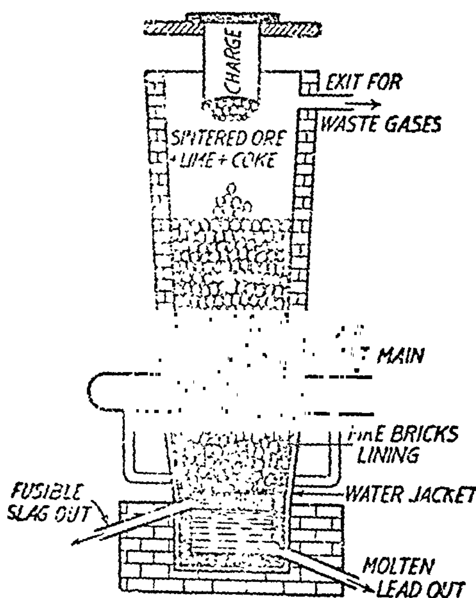
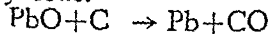


Fig. 57·4—Blast furnace for lead smelting.

Lead oxide is reduced by coke.

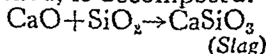


$$PbO + C \rightarrow Pb + CO$$

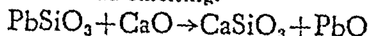


$$PbO + CO \rightarrow Pb + CO_2$$

Lime serves to remove silica as fusible slag and does not allow lead to be wasted as lead silicate, $PbSiO_3$ which even if formed, is decomposed.

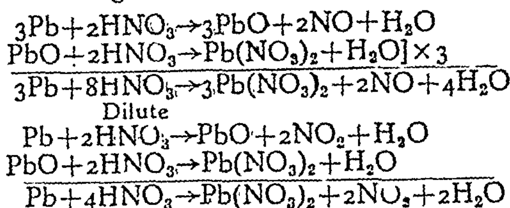


$$CaO + SiO_2 \rightarrow \underset{(Slag)}{CaSiO_3}$$



$$PbSiO_3 + CaO \rightarrow CaSiO_3 + PbO$$

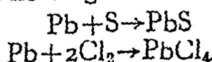
(*iv*) *Action of acids.* Hydrochloric acid and sulphuric acid have little effect upon lead but nitric acid reacts with it vigorously. Nitric oxide is evolved with the dilute acid while concentrated nitric acid liberates nitrogen dioxide.



$$3Pb+2HNO_3 \rightarrow 3PbO+2NO+H_2O$$
$$[PbO+2HNO_3 \rightarrow Pb(NO_3)_2+H_2O] \times 3$$
$$\overline{3Pb+8HNO_3 \rightarrow 3Pb(NO_3)_2+2NO+4H_2O}$$
Dilute
$$Pb+2HNO_3 \rightarrow PbO+2NO_2+H_2O$$
$$PbO+2HNO_3 \rightarrow Pb(NO_3)_2+H_2O$$
$$\overline{Pb+4HNO_3 \rightarrow Pb(NO_3)_2+2NO_2+2H_2O}$$

Acetic acid and some other organic acids react with lead.

(*v*) *Action of chlorine and sulphur.* Lead combines with chlorine and sulphur on heating.



$$Pb+S \rightarrow PbS$$
$$Pb+2Cl_2 \rightarrow PbCl_4$$

5. **Uses of Lead.**—(*i*) Lead is used for making lead pipes and containers for corrosive liquids.

(*ii*) Sheet lead is used for making lead chambers of sulphuric acid plant.

(*iii*) Underground telephone cables are protected by lead covering.

(*iv*) It is used in storage batteries.

(*v*) Large quantities of lead are used in preparing white lead, litharge and red lead.

(*vi*) It is used in many alloys.

6. **Alloys of Lead.**

(1) *Type metal* contains 82 per cent lead, 15 per cent antimony and 3 per cent tin. It is used for making types.

(2) *Solder.* It is an alloy of tin (50—57%) and lead (43—50%) used for soldering.

(3) *Pewter.* It is an alloy of variable composition and often contains 75 per cent tin and 25 per cent lead.

(4) *Fusible alloys.* These are alloys of lead with bismuth and tin and melt at low temperatures (below 100°C). Some of these are :

(*i*) *Wood's metal* (*m.p.* 60°C) contains bismuth 50%, lead 25%, tin 12·5% and cadmium 12·5%.

(*ii*) *Lipowitz alloy* (*m.p.* 60°C) contains bismuth 50%, lead 27%, tin 13% and cadmium 10%.

(*iii*) *Rose metal* (*m.p.* 80°C) contains bismuth 50%, lead 28% and tin 22%.

(iv) *Newton metal* (*m.p.* 94°*C*) contains bismuth 50%, lead 31% and tin 19%.

These are used for making soft solder, electric fuses, safety plugs for boilers and automatic water sprinklers (Fig. 57·5) to prevent fire. When a building catches fire, the heat melts the fusible alloy plug and water rushes out. This controls the fire automatically.

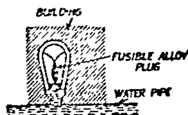


Fig. 57·5—Automatic water sprinkler.

COMPOUNDS OF LEAD

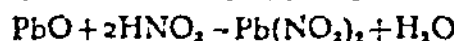
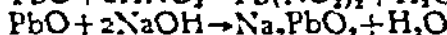
7. **Lead forms two Series of Salts.**—Lead gives two series of salts, *viz.*, the plumbous salts in which the metal is civalent and the plumbic salts in which lead is tetravalent. The former are stable while the latter are less stable and are either insoluble in water or hydrolysed in it. When plumbous or plumbic is not mentioned with a salt, plumbous is implied, *e.g.*, lead chloride means plumbous chloride.

8. **Lead Monoxide, PbO.**—It is obtained as a yellow powder called *massicot*, when lead is heated in air to about 300°C. At higher temperature (877°C), it fuses to give reddish yellow crystalline mass called litharge.


$$2Pb + O_2 \rightarrow 2PbO$$

Lead nitrate or carbonate on heating leaves lead monoxide. It is a by-product obtained during the purification of silver by cupellation process.

It is a yellowish grey powder which is insoluble in water. It is an amphoteric oxide and dissolves in acids as well as alkalis.


$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$$

$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$$

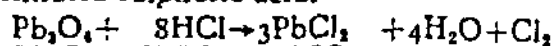
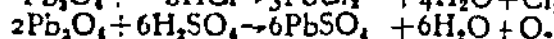
Uses. Lead monoxide is used in making glass; in the paint and varnish industries; in making lead salts and in glazing pottery. Massicot mixed with glycerine is employed as a cement for glass and stone.

9. **Red Lead, Pb_3O_4** (सिन्दूर).—Red lead is obtained when lead monoxide is heated to about 340°C in excess of air.


$$6PbO + O_2 = 2Pb_3O_4$$

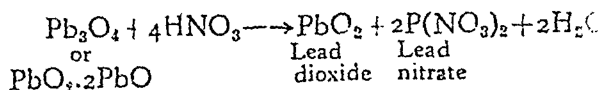
It is a red powder insoluble in water and decomposes on heating giving oxygen.

It oxidises hydrochloric acid to chlorine and gives oxygen with hot concentrated sulphuric acid.


$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2$$

$$2Pb_3O_4 + 6H_2SO_4 \rightarrow 6PbSO_4 + 6H_2O + O_2$$

This is considered to be a mixture of lead monoxide and lead dioxide ($PbO_2.2PbO$). The view is supported by the action of

nitric acid on the red lead when lead nitrate and lead di obtained.



$$\underset{\text{or } PbO_2.2PbO}{Pb_3O_4} + 4HNO_3 \longrightarrow \underset{\text{Lead dioxide}}{PbO_2} + \underset{\text{Lead nitrate}}{2P(NO_3)_2} + 2H_2O$$

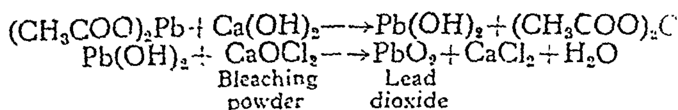
Uses. Red lead is used to make protective paint fo steel ; in glass and match industries ; and as an oxidising the laboratory.

10. **Lead Dioxide, PbO_2** (*or Peroxide of lea* obtained as a chocolate brown powder when red lead with nitric acid.



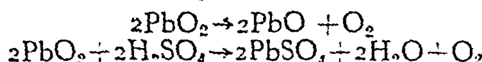
$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H$$

In the laboratory it is generally prepared by the of a lead salt with bleaching powder which contains son lime too.



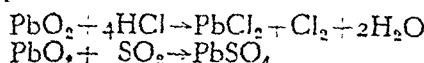
$$(CH_3COO)_2Pb + Ca(OH)_2 \longrightarrow Pb(OH)_2 + (CH_3COO)_2C$$
$$Pb(OH)_2 + \underset{\text{Bleaching powder}}{CaOCl_2} \longrightarrow \underset{\text{Lead dioxide}}{PbO_2} + CaCl_2 + H_2O$$

It is a powerful oxidising agent. It gives oxygen o alone or with concentrated sulphuric acid.



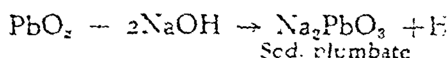
$$2PbO_2 \rightarrow 2PbO + O_2$$
$$2PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + O_2$$

It oxidises hydrochloric acid to chlorine and becom when sulphur dioxide is passed over heated lead dioxide. sulphur and phosphorus catch fire in contact with lead d



$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$
$$PbO_2 + SO_2 \rightarrow PbSO_4$$

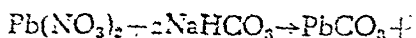
Lead dioxide is rather a weak acidic o. plumbates.



$$PbO_2 + 2NaOH \rightarrow \underset{\text{Sod. plumbate}}{Na_2PbO_3} + H$$

Uses. Lead dioxide forms the active m plate in storage cells and finds use in match oxidising agent.

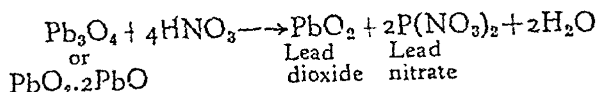
11. **Lead Carbonate, $PbCO_3$.**—It c In the laboratory it may be obtained by nate to the solution of a lead salt.



$$Pb(NO_3)_2 + 2NaHCO_3 \rightarrow PbCO_3 +$$

If instead of sodium bicarbonate w solution to the lead salt, the basic lead ca is precipitated. The basic lead carbonat tensively used in paints.

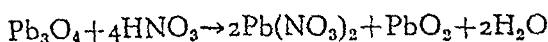
nitric acid on the red lead when lead nitrate and lead dioxide are obtained.



$$\underset{\substack{\text{or} \\ PbO_2.2PbO}}{Pb_3O_4} + 4HNO_3 \longrightarrow \underset{\substack{\text{Lead} \\ \text{dioxide}}}{PbO_2} + \underset{\substack{\text{Lead} \\ \text{nitrate}}}{2P(NO_3)_2} + 2H_2O$$

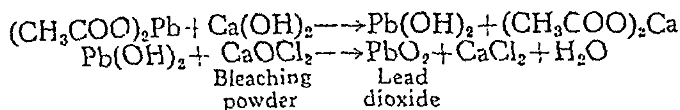
Uses. Red lead is used to make protective paint for iron and steel ; in glass and match industries ; and as an oxidising agent in the laboratory.

10. **Lead Dioxide, PbO_2** (*or Peroxide of lead*). It is obtained as a chocolate brown powder when red lead is treated with nitric acid.



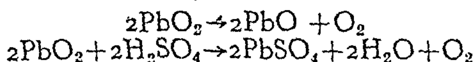
$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

In the laboratory it is generally prepared by the oxidation of a lead salt with bleaching powder which contains some slaked lime too.



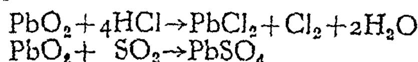
$$(CH_3COO)_2Pb + Ca(OH)_2 \longrightarrow Pb(OH)_2 + (CH_3COO)_2Ca$$
$$Pb(OH)_2 + \underset{\substack{\text{Bleaching} \\ \text{powder}}}{CaOCl_2} \longrightarrow \underset{\substack{\text{Lead} \\ \text{dioxide}}}{PbO_2} + CaCl_2 + H_2O$$

It is a powerful oxidising agent. It gives oxygen on heating alone or with concentrated sulphuric acid.



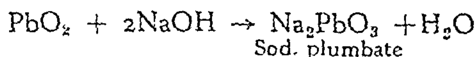
$$2PbO_2 \rightarrow 2PbO + O_2$$
$$2PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + O_2$$

It oxidises hydrochloric acid to chlorine and becomes red hot when sulphur dioxide is passed over heated lead dioxide. Powdered sulphur and phosphorus catch fire in contact with lead dioxide.



$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O$$
$$PbO_2 + SO_2 \rightarrow PbSO_4$$

Lead dioxide is rather a weak acidic oxide which forms plumbates.



$$PbO_2 + 2NaOH \rightarrow \underset{\text{Sod. plumbate}}{Na_2PbO_3} + H_2O$$

Uses. Lead dioxide forms the active material of the positive plate in storage cells and finds use in match industry and as an oxidising agent.

11. **Lead Carbonate, $PbCO_3$.**—It occurs native as *cerussite*. In the laboratory it may be obtained by adding sodium bicarbonate to the solution of a lead salt.



$$Pb(NO_3)_2 + 2NaHCO_3 \rightarrow PbCO_3 + 2NaNO_3 + CO_2 + H_2O$$

If instead of sodium bicarbonate we add sodium carbonate solution to the lead salt, the basic lead carbonate, $2PbCO_3, Pb(OH)_2$ is precipitated. The basic lead carbonate, called white lead, is extensively used in paints.

Manufacture. White lead is prepared on a commercial scale by two main processes, *viz.*, the older *Dutch Process* and the more recent *Carter Process*.

(i) Dutch Process. In this process, lead is melted and cast into the form of perforated discs called *buckles*. These are placed on shelves in small earthenware pots containing 3% acetic acid (Fig. 57·7). A number of such pots are stacked in a row over horse-dung or spent tan bark placed all round them. The row is covered with planks of wood and another row arranged over the planks, and so on. The pots are allowed to stand for about 6—8 weeks during which interval acetic acid vapour, moisture and carbon dioxide (from the fermentation of tan bark) all act upon lead and give flaky white lead. Various reactions taking place are :

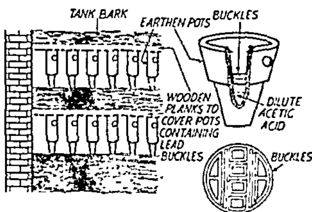
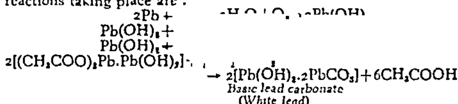


Fig. 57·6—Manufacture of white lead (*Dutch Process*).



$$2Pb + \quad \ldots$$
$$Pb(OH)_2 +$$
$$Pb(OH)_2 +$$
$$2[(CH_3COO)_2Pb.Pb(OH)_2] \ldots \rightarrow 2[Pb(OH)_2.2PbCO_3] + 6CH_3COOH$$

Basic lead carbonate
(White lead)

White lead is broken away from any unchanged lead, ground and washed with water to remove soluble lead acetate. It is then dried and the product is finely powdered.

(ii) Carter Process. In the Carter Process lead is melted, and atomized by spraying from nozzles by means of compressed air or steam. The finely divided lead is taken in wooden barrels which can be rotated about their axes. A spray of acetic acid, carbon dioxide and air are blown into the barrels. The chemical reactions taking place are the same as given under the Dutch process. The conversion occurs in 5—12 days and gives a product which is whiter, finer and more uniform than obtained by the other process.

Properties and Uses. It is a white paint with good covering power, which darkens by the action of hydrogen sulphide due to the formation of lead sulphide. It is used as a white paint

12. **Tests for Lead**—(i) *Charcoal cavity test.* When a lead salt is heated with sodium carbonate in a charcoal cavity, it gives a yellow incrustation (brown when hot and yellow when cold) and a white malleable bead which marks paper black.

(*ii*) *With dilute hydrochloric acid*, lead salts give a white precipitate which dissolves in water on boiling and reappears on cooling.

(*iii*) *Hydrogen sulphide* gives a black precipitate of lead sulphide which is insoluble in yellow ammonium sulphide but dissolves in 50 per cent nitric acid.

(*iv*) *Dilute sulphuric acid* produces with a lead salt a white precipitate of lead sulphate soluble in ammonium acetate.

(*v*) *Potassium iodide* gives a yellow precipitate of lead iodide which dissolves in water on boiling but crystallizes on cooling.

(*vi*) *Potassium chromate*, when added to a lead salt acidified with acetic acid, gives a yellow precipitate of lead chromate.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Galena+(*i*) Lead oxide (heated) ; (*ii*) Lead sulphate (heated).
2. Lime+(*i*) Sand ; (*ii*) Lead silicate.
3. Lead+(*i*) Nitric acid (dil. and conc.) ; (*ii*) Chlorine ; (*iii*) Sulphur.
4. Red Lead+(*i*) Hydrochloric acid ; (*ii*) Concentrated sulphuric acid ; (*iii*) Nitric acid.
5. Lead acetate+Bleaching powder.
6. Lead dioxide+(*i*) Conc. sulphuric acid ; (*ii*) Hydrochloric acid ; (*iii*) Sulphur dioxide ; (*iv*) Caustic soda ; (*v*) Heated.
7. Lead nitrate+(*i*) Sodium bicarbonate ; (*ii*) Heated ; (*iii*) Hydrochloric acid.
8. Lead+Dil. acetic acid+Carbon dioxide+Air.
9. Lead sulphate+Ammonium acetate.

QUESTIONS

1. How is lead obtained from galena ? Give two important uses of lead metal. (*Punjab Pre-Univ. 1963 ; Delhi H.S. 1969 ; Delhi Pre-Medical 1960*)

2. What are the naturally-occurring ores of lead ? Describe the process of obtaining metallic lead from its common ore. How are different oxides of lead prepared ? Give their uses. (*Delhi H.S. 1971, 70*)

3. Give the preparation, properties and uses of any two of the following :

(*i*) White lead. (*All India H.S. 1966 ; Delhi H.S. 1972, 70, 61*)

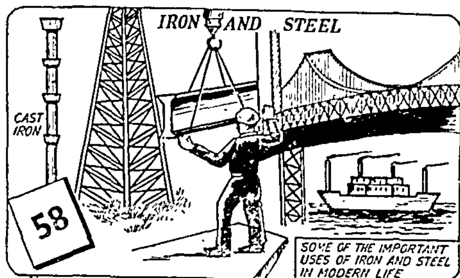
(*ii*) Red lead. (*Punjab Pre-Univ. 1963*)

(*iii*) Lead dioxide. (*Delhi H.S. 1965 ; Delhi Pre-Medical 1963*)

4. Write short notes on :

(*a*) Desilverization.

(*b*) Use of lead and its compounds.



The Iron Group

1. General.—The iron group includes iron, cobalt and nickel, the transition elements of the first long period placed in Group VIII of the Periodic Table. Their inclusion in the same group is justified by their common characteristics as given below :

(i) They are all hard metals with high melting and boiling points, as given in the table of their physical constants below :

Element	Atomic weight	Atomic number	Electronic arrangement	Specific gravity	Melting point	Boiling point
Iron	55 85	26	2, 8, 14, 2	7 86	1535°C	3000°C
Cobalt	58 94	27	2, 8, 15, 2	8 90	1480	2900
Nickel	58 69	28	2, 8, 16, 2	8 90	1452	2900

(ii) They are all magnetic in character.

(iii) All of them occur as sulphides which are associated with each other.

(iv) There is a regular gradation in their chemical properties also. For example, iron forms two series of salts, *viz.*, ferrous and ferric, both stable. Cobalt gives stable cobaltous salts and unstable cobaltic salts. In the case of nickel only nickelous salts are known Thus they show a variable valency.

(v) All of them decompose steam when passed over red hot metals.

(*vi*) When dipped in concentrated nitric acid, they become passive.

(*vii*) With carbon monoxide they give volatile carbonyls.

(*viii*) They are used as catalysts in hydrogenation reactions. The use depends upon their property of absorbing hydrogen.

(*ix*) All of them give complex ions, *e.g.*, ferricyanide, $Fe(CN)_6^{3-}$; cobaltinitrite, $Co(NO_2)_6^{3-}$ and nickelocyanide, $Ni(CN)_4^{2-}$.

(*x*) Their salts are isomorphous, *e.g.*, ferrous ammonium sulphate (Mohr's salt), $FeSO_4.(NH_4)_2SO_4.6H_2O$ and nickel ammonium sulphate, $NiSO_4.(NH_4)_2SO_4.6H_2O$.

IRON

2. **Historical.**—Iron articles were made by the Egyptians and Syrians as early as 3000 B.C. Indians had specialised in the metallurgy of iron and manufacture of steel. Ashoka's iron pillar in Delhi and the iron joints used in the temple of Puri, made of stainless steel, as they are, speak of the glory of our skill in this art.

Blast furnaces for the smelting of iron were introduced in Germany in about 1350 and in Great Britain in about 1500. Charcoal was the first reducing agent employed but coal and coke were used later.

3. **Occurrence.**—Small quantities of iron occur native. It is also found in many meteorites as an alloy with 3—8 per cent of nickel. Its most abundant ore is *haematite*, Fe_2O_3, a reddish brown ore. Some others are : *Limonite*, $2Fe_2O_3.3H_2O$—a hydrated oxide of iron, *Magnetite*, Fe_3O_4—a magnetic oxide and *Siderite*, $FeCO_3$—the spathic iron ore. The commercial value of an ore depends not only on its iron content, which varies between 25% and 65% approximately, but also upon the absence of objectionable impurities such as phosphorus, sulphur, arsenic and titanium. For example, iron pyrites, FeS_2 although very abundant, is not an ore of iron. It is used in the manufacture of sulphuric acid as a source of sulphur dioxide.

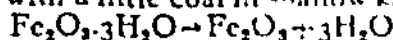
Huge deposits of *haematite* are available in India in Mayurbhanj, Singbhum and Mysore. It is worked for the manufacture of iron and steel at Asansol, Jamshedpur, Bhadravati and other places.

4. **Commercial forms of Iron.**—Iron ore is worked for the manufacture of three chief varieties of iron, *viz.*, *cast iron*, *wrought iron* and *steel*. The three varieties differ from each other mainly in their carbon content. Cast iron and pig iron contain 2—5 per cent of carbon as well as other impurities. Wrought iron is the purest form of iron which is used commercially. Carbon content of steel (0·2—2 per cent) is more than that of wrought iron as a rule, and less than that of cast iron. The first step in the metallurgy of iron is the manufacture of pig iron which is further used in the preparation of iron and steel.

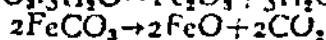
5. **Manufacture of Cast Iron.**—The extraction of iron from any of the above ores involves the following processes:

(1) **Dressing of the ore.** Before smelting it is necessary in most cases to subject the iron ore to preliminary process. The ore is broken into small pieces of 1-2" size, screened and sifted. Most of the ores are rich enough and do not need any concentration. It is only in a few cases that the ore is washed with water.

(2) **Preliminary roasting or calcination.** The ore after washing is roasted with a little coal in shallow kilns in excess of air.



$$Fe_2O_3 \cdot 3H_2O \rightarrow Fe_2O_3 + 3H_2O$$



$$2FeCO_3 \rightarrow 2FeO + 2CO_2$$



$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

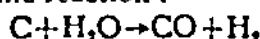
(i) This ensures the removal of moisture, carbon dioxide, sulphur and arsenic. Thus it lowers the sulphur content of the ore.

(ii) It results in conversion of ferrous oxide into ferric oxide which would not form slag with sand (ferrous oxide gives ferrous silicate).

(iii) In addition to these chemical changes, it makes the mass porous thus making it more suitable for ready reduction to metallic iron.

(3) **Smelting in a Blast furnace.** Blast furnace used is a chimney-like structure made of iron plates lined inside with fire-bricks (Fig. 58·1). It is about 90 feet high with a maximum diameter of about 25 feet and is provided at the top with a *cup and cone arrangement*. Thus charge can be fed at the top while no gases escape from inside.

Roasted ore (8 parts) with desulphurised coke (4 parts) and limestone pieces (1 part) is fed into the upper bell. This upper bell is lowered to allow the charge to fall onto the lower bell which in the meanwhile is held against its hopper. The upper bell is then raised and the lower bell lowered when the charge falls into the body of the furnace but no gas escapes. Air is blown in through water-jacketed pipes called *tuyeres* fixed in the lower part of the furnace. To effect fuel economy the blast is pre-heated in the Cowper stove by the combustion of part of the furnace exit gases. The air used is also sometimes dried by means of silica gel so as to reduce the cooling effect of the endothermic reaction:



$$C + H_2O \rightarrow CO + H_2$$

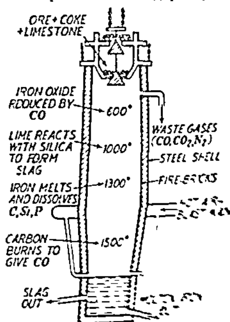


Fig. 58·1—[illegible]

The movement of these materials through the blast furnace is shown in Fig. 58·1 whereas the general arrangement of the blast furnace and its subsidiary plants is shown in Fig. 58·2. The various chemical reactions going on in the blast furnace are :

Fig. 58·2—General arrangement of the Blast furnace and its subsidiary plants.

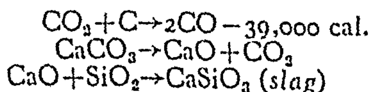
(*a*) In the lower part, called **Zone of Fusion**, coke burns to carbon dioxide producing lot of heat.



$$C+O_2 \rightarrow CO_2+97,000 \text{ cal.}$$

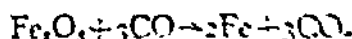
Here the temperature is 1500°C. A little above this the temperature prevailing is 1200—1300°C and it is here that porous iron sliding down from above melts. Any oxide, which might have escaped reduction, is also reduced by coke.

(*b*) In the middle part of the furnace called **Zone of heat absorption** (Temp. 800—1000°C), carbon dioxide rising up is reduced to carbon monoxide accompanied by heat absorption. Limestone sliding down decomposes to give lime and carbon dioxide. Lime thus obtained acts as *flux* and combines with silica (present as impurity—*gangue*) to form calcium silicate (*fusible slag*).



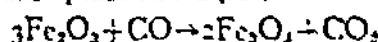
$$CO_2+C \rightarrow 2CO-39,000 \text{ cal.}$$
$$CaCO_3 \rightarrow CaO+CO_2$$
$$CaO+SiO_2 \rightarrow CaSiO_3 \ (slag)$$

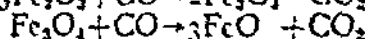
(c) At the top is the **Zone of Reduction** (Temp. ...). Here iron oxide is reduced to spongy iron by carbon monoxide rising up.

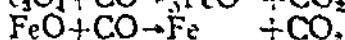


$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

It is suggested that reduction of ferric oxide, Fe_2O_3 by carbon monoxide takes place in stages :







$$3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$

At the bottom of the furnace the molten iron sinks down while above this floats the fusible slag which protects the molten iron from oxidation. Molten iron and slag are tapped from different holes as shown.

Although the overall result of smelting is clear that iron oxide is reduced to iron and the silica present forms a slag with limestone, the mechanism by which reduction takes place is still a matter of controversy. Conditions in the blast furnace cannot be imitated in the laboratory and it is not possible to obtain representative samples from different zones of the furnace in operation. Small experimental furnaces were constructed and cooled to examine the contents of different zones. It is doubtful that these contents after long periods of cooling represented the contents while the furnace was in blast.

It is almost certain ... oke is burnt to car- ... ably in stages with ... ittle, if any, of the

At about 450°C. carbon monoxide disproportionates rapidly into carbon dioxide and carbon and the change is catalysed by iron and its oxides. Due to this ore gets impregnated with carbon to a greater or lesser extent. As this impregnated ore slides into a zone of higher temperature, direct reduction of the ore by carbon may take place with or without the intervention of lower oxides. But this view is not universally accepted.

Waste gases escaping at the top consist of about 30 per cent CO, 10 per cent CO_2 and the rest nitrogen. The mixture is called *blast furnace gas*. It is cleaned by passing through a dust catcher, mixed with sufficient air and burnt in a Cowper stove, a tower packed with a chequer-work of firebricks. When a Cowper stove has been heated, it is used for pre-heating the blast of air to be blown into the blast furnace. As this Cowper stove is being cooled, the blast furnace gas is burnt in the second stove.

Iron thus obtained is called **Pig Iron**. Solid pig iron on remelting in a vertical furnace, heated by coke and known as a *cupola*, can be cast or poured into moulds. Hence after remelting it is known as **Cast iron**.

6. **Properties of Cast Iron.**—Pig iron and cast iron contain 2—5 per cent of carbon as well as other impurities (usually silicon, manganese, sulphur and phosphorus). The carbon is present either as free carbon in the form of graphite or in the combined state as *cementite* (iron carbide Fe_3C). **White cast iron** *contains cementite and is obtained by cooling the molten pig iron quickly.* **Grey cast iron** *contains more graphite and is obtained by cooling it slowly.*

It is very hard but brittle and cannot be welded. It expands on solidification and is used for casting various articles such as stoves, pipes, radiators and toys. It does not easily rust when exposed to air and is, therefore, used in making gutter pipes and lamp-posts.

7. **Manufacture of Wrought Iron.**—It is the purest form of iron and is prepared by heating cast iron in a reverberatory furnace lined with iron oxide (Fig. 58·3). The hot gases and flames are deflected by the low roof down on the charge placed in the bed of the reverberatory furnace. The carbon present in the cast iron is oxidised by the iron oxide lining and the other impurities either unite with the basic lining or are slagged off. The slag is removed by hammering the plastic iron gathered in balls on the ends of iron rods used for stirring or *puddling* the molten metal.

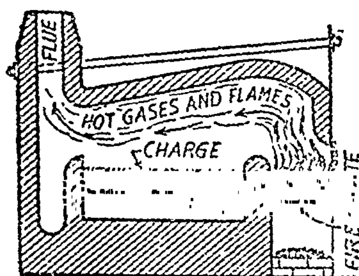


Fig. 58·3—Reverberatory furnace used for the manufacture of wrought iron.

Wrought iron contains only about 0·2 per cent of carbon. It is an extremely tough and tenacious metal with a high melting point. It has a fibrous structure due to the presence of slag between its different layers. It can withstand sudden stress and is used in making anchors, chains, nails and fire-bars.

8. **Manufacture of Steel.**—Steel is iron with a carbon content intermediate between cast iron and that of wrought iron. It contains 0·2—2 per cent of carbon and manganese. Steel is used for (*i*) making machinery parts, girders, tools, springs, dies, needles, surgical instruments and cutlery; and (*ii*) preparing permanent magnets and magnetic needles. Steels containing other elements such as chromium, nickel, tungsten, molybdenum, vanadium and silicon are called *Alloy steels*. Several processes for making steel are :

(*a*) **Cementation Process.** In this process bars of wrought iron are packed in powdered charcoal and heated for several days. Steel is obtained by slow penetration of carbon particles into the wrought iron.

(*b*) **Crucible Process.** In the crucible process, now almost obsolete, steel was prepared by melting wrought iron with

charcoal in a closed fireclay-graphite crucible. It yielded steel of very high quality but in small batches only.

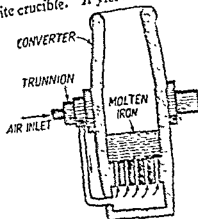


Fig. 58·4—A Bessemer converter, during the time of air blast.

(c) The Bessemer Process. Molten pig iron is taken in a Bessemer converter (Fig. 58·4), a pear-shaped furnace lined with silica (Acid Bessemer Process) or lime (Basic Bessemer Process) when phosphorus is present as impurity. It is big enough to hold 15–20 tons of pig iron and is mounted on trunnions which render it capable of being tilted in any position.

To start with, the converter is turned on its side to receive the charge of molten pig iron (Fig. 58·5). It is now brought almost to a vertical position (Fig. 58·4) and a blast of air passed in. Carbon and various other impurities present combine with oxygen forming products which are either slagged off by the lining or escape as gases.

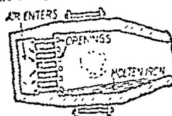
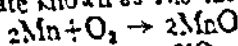


Fig. 58·5—Bessemer converter during the time it receives its charge of molten pig iron.

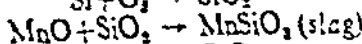
At first manganese and silicon present are removed as slag. Similarly phosphorus in Basic process is slagged off as calcium phosphate known as Thomas slag, generally used as a fertilizer.



$$2Mn + O_2 \rightarrow 2MnO$$



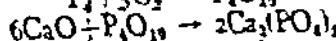
$$Si + O_2 \rightarrow SiO_2$$



$$MnO + SiO_2 \rightarrow MnSiO_3 \text{ (slag)}$$



$$P_4 + 5O_2 \rightarrow P_4O_{10}$$



$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

(Thomas slag)

This is followed by oxidation of carbon to carbon monoxide which burns at the mouth of the converter (Bessemer's candles) till it is finished and flame dies out. Requisite amount of carbon is now added as spiegeleisen (an alloy of iron with 5–15% manganese and 60% of carbon). The manganese added in the form of spiegeleisen or ferro-manganese unites with oxygen left in the steel from the blast of air and thus prevents the formation of blow-holes. Some aluminium or ferro-silicon may be added to remove blow-holes.



[illegible]

(*d*) **Open Hearth Process.** This process differs from the Bessemer process in the following respects :

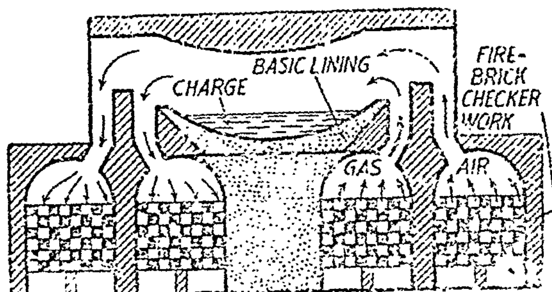
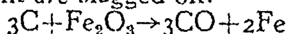


Fig. 58·6—An open hearth furnace.

(*i*) Impurities present in cast iron are oxidised by adding iron ore and not by air as in the Bessemer process.

(*ii*) Percentage of carbon and silicon is lowered by adding low-grade wrought iron and scrap steel.

Pig iron is mixed with about 25—40% of its weight of scrap iron, low grade wrought iron and haematite and taken in an open hearth lined with magnesia bricks or silica as desired depending upon the nature of the impurities present. It is heated in a gas fired furnace working on regenerative principle of heat economy (Fig. 58·6). *Carbon is oxidised by haematite present* while impurities present are slagged off.



$$3C + Fe_2O_3 \rightarrow 3CO + 2Fe$$

Samples of the charge are drawn out from time to time and analysed for carbon content. When a test shows that the metal contains the right amount of carbon, ferro-manganese and aluminium are added as in the Bessemer process.



Jamsetji Nusserwanji Tata
(1839—1904)
Indian industrialist and founder of the Tata Iron and Steel Company Ltd. He did the pioneering work in Iron and Steel Industry. He founded the Institute of Science, Bangalore.

The Open Hearth process has the following advantages over the Bessemer process.

(*i*) The steel obtained is superior in quality as during the process of heating the composition of the product could be controlled.

(*ii*) Another advantage of this process is that iron ore, scrap iron and low-grade pig iron can be used.

(*iii*) No blast of air is passed, hence practically no iron is lost by slag formation.

(*e*) **Electric Steel.** Very fine steel is manufactured in an electric furnace. One commonly used electric furnace is Heroult's furnace shown in Fig. 58·7. It consists of a steel shell lined inside with basic lining of dolomite or magnesite and provided with movable and water-jacketed electrodes coming in from the roof or

from the sides. The charge consists of scrap steel, cast iron and iron ore. On striking the electric arc between the electrodes the high temperature is produced due to which the charge melts. The impurities present in the charge (*e.g.*, Si, Mn, P, S) combine with basic lining to form slag. The steel obtained is free from sulphur and gas bubbles. Since high temperatures are possible in the electric furnace, alloy steels with high melting points are manufactured by this process. High grade steel is obtained by this process :

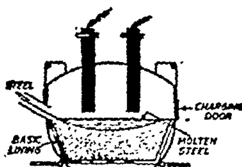


Fig. 58·7—Heroult's furnace.

(i) Steel is tested at various intervals before it is finished.
(ii) Raw materials used in the process are usually purer.
(iii) Oxidation of steel is prevented by carrying on the operation in a reducing atmosphere.

Iron and Steel Industry in India. Iron and steel is being manufactured [illegible] d Steel [illegible] adravati, [illegible] ilai and [illegible] steel plant [illegible]

	Capacity			Production		
	1960-61	*1965-66*	*1970-71*	*1960-61*	*1965-66*	*1970-71*
Steel ingots	6,000	9,200	21,000	3,300	7,800	[illegible]
Finished mild steel	4,550	6,500	13,500	2,450	5,800	[illegible]
Steel castings & forgings	83·6	300	1,200	70·4	300	[illegible]
Steel pipes & tubes	365	518	1,200	112	417	[illegible]
Pig iron	6,400	9,000	20,000	4,000	[illegible]	[illegible]
Grey iron castings	—	1,000	2,500	—	[illegible]	[illegible]
Cast iron pipes	275	609	1,400	213	[illegible]	[illegible]

9. **Heat Treatment of Steels.**

(i) **Annealing.** *It is the process of heating* [illegible] *red heat and then cooling it slowly.* By annealing steel [illegible] soft and pliable. It wears better than wrought iron [illegible]

(ii) **Hardening.** *It is the process of heating* [illegible] *redness and then cooling suddenly by plunging* [illegible] (*Quenching*). Steel so treated is hard and brittle.

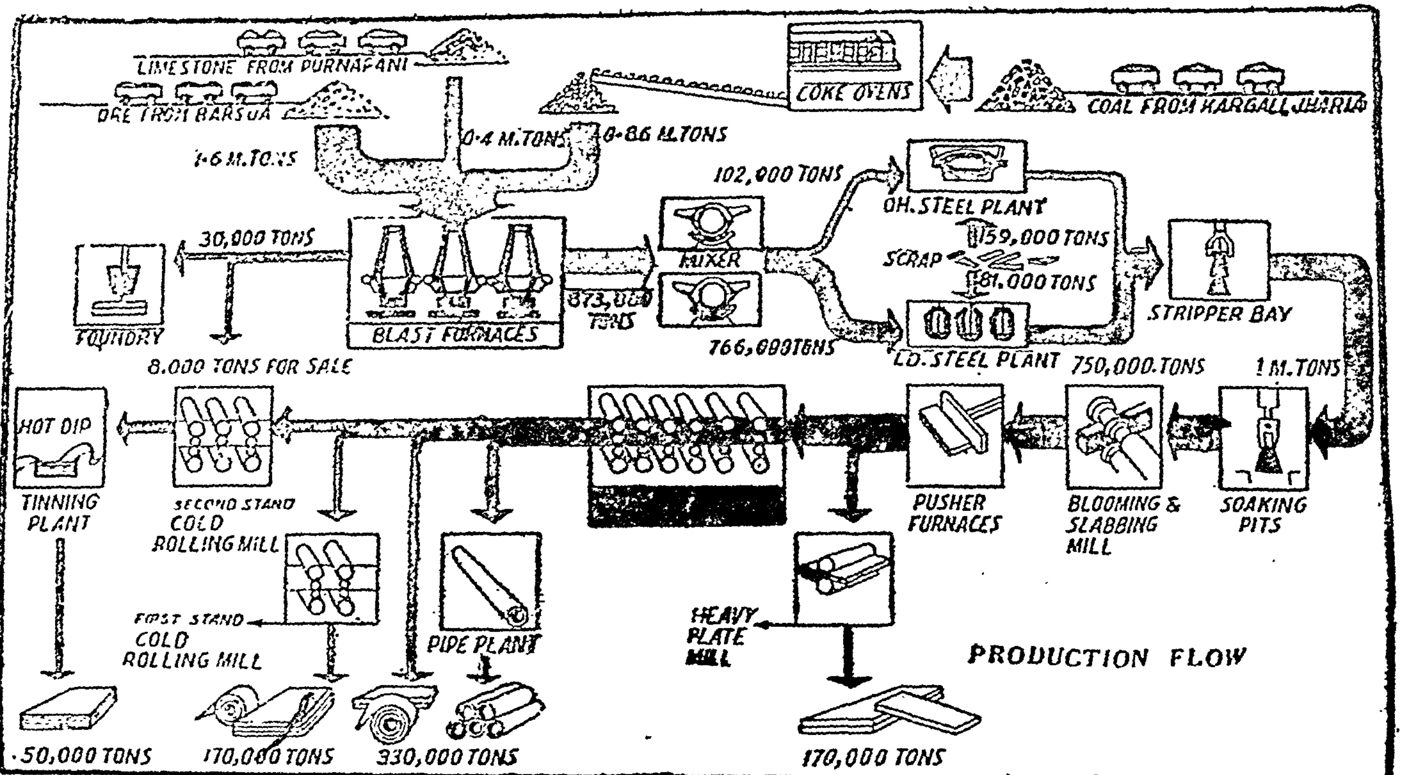


Fig. 58·8—A diagram showing the flow of production at the Rourkela Steel Works.

(iii) Tempering. *It is the process of heating the hardened steel to a temperature much below redness and cooling it slowly.* The product obtained is neither so hard nor so brittle.

(iv) Case-hardening. *It is the process of giving a thin coating of hardened steel to a strong, flexible, mild steel by heating it in contact with charcoal and quenching in oil.*

Thus due to hardened surface layer it can stand wear and tear. The inside, being still mild steel, can withstand shock. Locomotive axles are made of case-hardened mild steel.

(v) Nitriding. *It is the process of heating steel in an atmosphere of ammonia when the surface is coated with hard iron nitride.*

10. Classification of steels.

(*a*) Mild Steel. It is a variety of steel containing smaller percentage of carbon. It possesses the properties of wrought iron alone with elasticity and hardness of steel.

(*b*) Hard Steel. Hardness of steel depends upon its carbon content and steel containing larger percentnges of carbon is hard and brittle like glass. Mild steel may be hardened by *quenching*.

(*c*) Alloy Steel. Very useful and valuable properties may be imparted to steel by alloying it with other metals, *e.g.*, nickel, cobalt, chromium, etc. All these alloys of steel are called alloy steels. Composition and uses of various alloy steels in industry are given below :

Alloy steel	Composition	Uses
1. Nickel steel	3·5% Ni.	In making cables, propeller shaft, automobile and aeroplane parts, armour plates, etc
2. Chrome Steel	1·5—2% Cr.	For preparing armour-piercing projectiles, crushing machinery and cutlery.
3. Chrome vanadium steel	0·15% V ; 1% Cr.	In manufacturing springs, axles, shafts and motor car frames
4. Manganese steel	12—15% Mn.	For making rock-crushing machinery, armour-plates burglar-proof safes, rail-road tracks, etc.
5. Tungsten steel	14—20% W ; 3—8% Cr.	For high speed tools
6 Invar	36% Ni.	For making measuring instruments and clock pendulums
7. Stainless steel	11·5% Cr.	Cycle and automobile parts.

(*d*) Steel containing sulphur and phosphorus. Iron or steel containing excessive quantities of sulphur is brittle while hot (*hot short*) whereas excessive quantities of phosphorus make it brittle while cold (*cold short*).

11. Common forms of Iron

Name	Approx. M.P.	Structure	Hardness	Ductile	Malleable	Tenacious	Tempered	Welded
1. Wrought iron	1500°C	Fibrous	Soft	Yes	Yes	Yes	No	Yes
2. Mild steel	1400—1500	Granular	Moderately soft	,,	,,	,,	,,	,,
3. Hard steel	1300—1400	,,	Hard to very hard	Not much	Not much	,,	Yes	With difficulty
4. Cast iron	1150—1250	Crystalline	Very hard	No	No	Not much	No	No

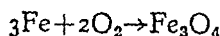
12. Properties of Iron.—(*a*) Pure iron is a silver-white metal. Physical properties its commercial forms are given in the table given above.

(*b*) *Rusting of iron.* Rust is a mixture of ferric oxide with a little ferric hydroxide. Iron gets rusted by the combined action of water, air and carbon dioxide and its life is shortened thereby. Rusting can be prevented by either of the following ways :

(*i*) Giving it a protective coating of metal like copper, nickel, chromium, zinc, tin or aluminium. This may be done by electroplating or otherwise.

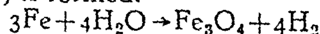
(*ii*) By covering its surface with paints or enamels.

(*c*) *Action of oxygen.* Red hot iron burns in oxygen giving sparks.



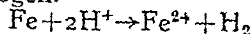
$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

(*d*) *Action of water.* When steam is passed over red hot iron, hydrogen is liberated and magnetic oxide of iron, Fe_3O_4 (Ferrosoferric oxide) is formed.



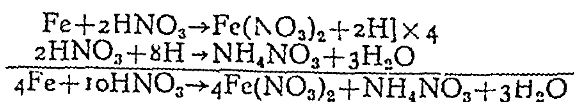
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

(*e*) *Action of acids.* From dilute hydrochloric and sulphuric acids it displaces hydrogen.



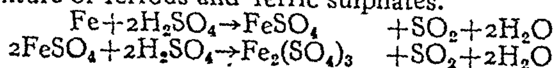
$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$$

With dilute nitric acid, it gives ferrous nitrate and ammonium nitrate.



$$[Fe + 2HNO_3 \rightarrow Fe(NO_3)_2 + 2H] \times 4$$
$$2HNO_3 + 8H \rightarrow NH_4NO_3 + 3H_2O$$
$$4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$$

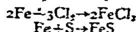
With hot concentrated sulphuric acid, it gives sulphur dioxide and a mixture of ferrous and ferric sulphates.



$$Fe + 2H_2SO_4 \rightarrow FeSO_4 + SO_2 + 2H_2O$$
$$2FeSO_4 + 2H_2SO_4 \rightarrow Fe_2(SO_4)_3 + SO_2 + 2H_2O$$

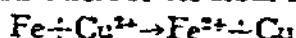
Moderately concentrated nitric acid dissolves iron giving ferric nitrate and liberates oxides of nitrogen. It does not dissolve in fuming nitric acid and its surface is changed in such a way that it fails to exhibit the properties of normal iron. It is said to be passive.

(*f*) *Action of alkalis, halogens and sulphur.* Alkalis have no action on iron. Halogens and sulphur combine with the heated metal forming halide and sulphide respectively.



$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$
$$Fe + S \rightarrow FeS$$

(*g*) *Displacement of less electropositive metals.* It displaces metals lower in electrochemical series from their salt solutions.



$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$$

13. **Passivity.**—*Place a piece of iron in dilute sulphuric acid,* a vigorous reaction begins and hydrogen gas starts coming out. The same piece of iron will displace copper from a solution of copper sulphate. It is noticed, however, that if the iron piece be first kept for some time in concentrated nitric acid and then washed free from nitric acid, it can neither liberate hydrogen from dilute sulphuric acid nor precipitate copper from copper sulphate solution. In other words, by treatment with concentrated nitric acid iron has so changed that it would not behave in the same manner as an ordinary piece of iron would do. Similar behaviour is shown by chromium, nickel, aluminium and some other metals.

This inertness exhibited by metals under conditions in which chemical activity is to be expected is called Passivity.

Since iron can be rendered passive not only by nitric acid but also by other oxidising agents like chromic acid, acidified potassium permanganate solutions, etc., the cause of this phenomenon is the *formation of a thin film of oxide* on the surface of the metal and this oxide film prevents the further corrosion of the metal.

According to Evans this oxide film is very thin and transparent so that it is quite invisible ordinarily. If this is removed mechanically or chemically, the metal becomes active again. Thus *passive iron* when heated in dilute nitric acid up to 75°C, becomes active again and begins to dissolve in nitric acid.

In electroplating or electrolysis the anodes sometimes become passive if a high current density is employed or when a strong oxidising agent is present in the solution.

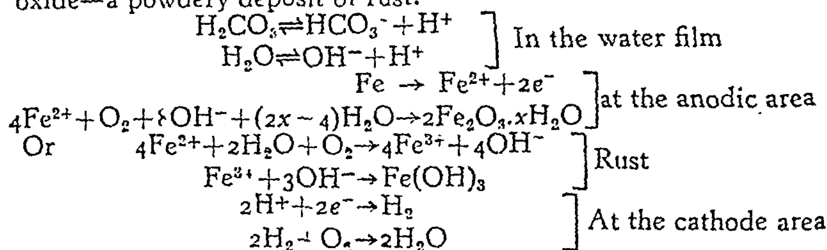
14. **Rusting of Iron.**—Rust is a mixture of ferric hydroxide, $Fe(OH)_3$ and ferric oxide, Fe_2O_3 and is produced by the action of water on iron in presence of dissolved oxygen and sometimes also carbon dioxide. A number of theories have been put forward to explain the phenomenon of rusting out of which the electro-chemical theory is more probable.

According to this, it is believed the chemically non-uniform surfaces of commercial forms of iron and steel behave like small

electric cells (or corrosion couples) in presence of water containing dissolved oxygen and carbon dioxide. The layer of liquid water on the surface of the moist iron dissolves oxygen and carbon dioxide. In polluted atmospheres of industrial areas and on ships or near the sea some sulphur dioxide is also absorbed. Thus the metal is soon in contact with a solution of the electrolyte and a chemical depolarizer.

In the initial stages of rusting, ferrous ions (Fe^{2+}) pass into solution at the anodic areas while hydrogen ions (H^+) originating from the water or suitable electrolytes (*e.g.*, H_2CO_3) are discharged at the cathodic areas. The other ions (OH^- and HCO_3^-) migrate to the anodic area.

Dissolved oxygen oxidizes hydrogen to water at the cathode and thus acts as a depolarizer. It oxidizes ferrous ions to ferric ions at the anode. Hydroxyl ions present at the anode combine with Fe^{3+} ions there forming ferric hydroxide or hydrated ferric oxide—a powdery deposit of rust.



$$\left.\begin{array}{c} H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \\ H_2O \rightleftharpoons OH^- + H^+ \end{array}\right] \text{In the water film}$$

$$\left.\begin{array}{c} Fe \rightarrow Fe^{2+} + 2e^- \\ 4Fe^{2+} + O_2 + 8OH^- + (2x-4)H_2O \rightarrow 2Fe_2O_3.xH_2O \end{array}\right] \text{at the anodic area}$$

$$\text{Or} \quad \left.\begin{array}{c} 4Fe^{2+} + 2H_2O + O_2 \rightarrow 4Fe^{3+} + 4OH^- \\ Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \end{array}\right] \text{Rust}$$

$$\left.\begin{array}{c} 2H^+ + 2e^- \rightarrow H_2 \\ 2H_2 + O_2 \rightarrow 2H_2O \end{array}\right] \text{At the cathode area}$$

Rust is a secondary product and does not adhere to the surface. It affords, therefore, no protection for the metal surface. Instead, it promotes further corrosion by excluding oxygen. Process of rusting is depicted schematically in Fig. 58·9.

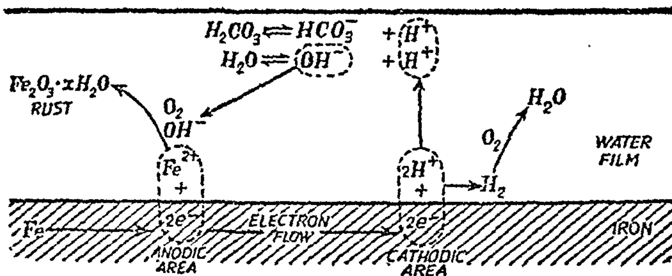


Fig. 58·9—Schematic representation of the process of rusting.

Prevention of rusting. Iron and steel are so widely used that the fight against rusting is of paramount importance. Iron is protected from rusting by one or more of the following methods :

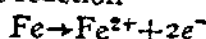
(*i*) Protection by metallic coatings which are more resistant to corrosion such as of tin, nickel, zinc, chromium, aluminium, etc.

(*ii*) Protection by oxide (*e.g.*, Fe_3O_4), phosphate (*e.g.*, $FePO_4$) or other chemical coatings. Application of solutions containing phosphoric acid and orthophosphates produces an insoluble tenacious film of iron phosphate.

(iii) Films of oil and grease are used on tools and machinery to prevent rusting.

(iv) Protection by paint, lacquers and enamels. Vitreous enamels prevent rusting and may also be decorative.

Protective action of Zinc. Thin coating of zinc in galvanized iron does not allow iron to come in contact with air and moisture and hence protects it from rusting. Even when the protective zinc coating is broken, iron is protected because zinc lies above iron in the activity series and is thus more electropositive than iron. Hence in this case it is zinc which tends to lose electrons not iron. Thus the reaction



$$Fe \rightarrow Fe^{2+} + 2e^-$$

necessary for rusting does not occur.

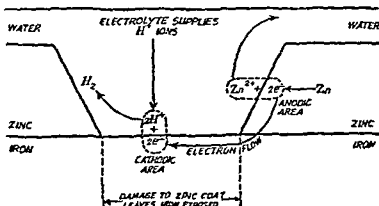


Fig. 58·10 —Protective action of zinc in a galvanized iron sheet

-ons,
the
d in

the protection of iron. At areas where the surface coating is undamaged, zinc is protected from corrosion by firmly adhering layer of zinc oxide.

Protective action of Tin. Tin is resistant to corrosion, hence a thin coating of tin over iron protects it from rusting. Tin coating, however, is not so durable as that of zinc in galvanized iron. Moreover when the layer of tin is broken and some iron surface exposed, rusting is more rapid than of an unprotected iron piece. This is because iron stands above tin in the activity series and is, therefore, more electropositive than tin. Iron, therefore, easily loses electrons and rusting is facilitated.

Thus at the exposed iron surface (anodic area) ferrous ions pass into solution. These Fe^{2+} ions are oxidized to Fe^{3+} ions by

dissolved oxygen and produce rust as explained before. The protective action of tin is represented schematically in Fig. 58·11.

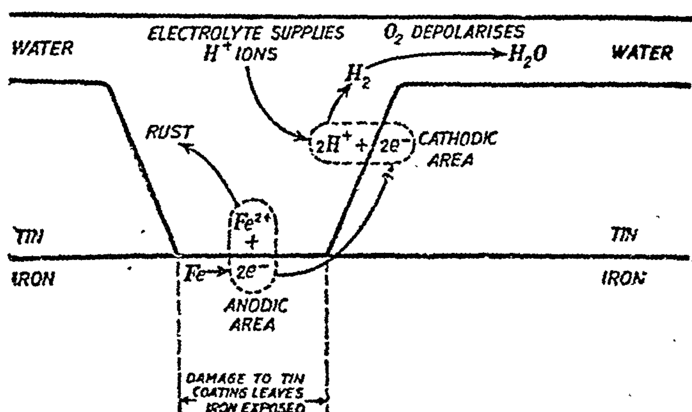


Fig. 58·11—Protective action of tin in a tin-plate.

Tin-plate is used in canning food. As long as the coating is not damaged, tin being more resistant to corrosion withstands the action of acids present in fruit juice, etc When damage to the surface has occurred, iron passes into solution and no poisonous tin compound passes into solution.

Galvanized iron containers cannot be used for the purpose because zinc will pass into solution forming poisonous zinc salts which will poison the contents.

COMPOUNDS OF IRON

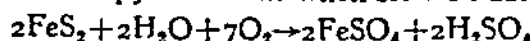
15. **General.**—Iron forms two series of compounds: (i) *Ferrous compounds* containing divalent electro-positive iron, and (ii) *ferric compounds* in which the metal is trivalent electro-positive. General characteristics of the two series of compounds are summarized in the table below.

Property	Ferrous Compounds	Ferric Compounds
1. Colour	Anhydrous—White Hydrated—Light green	White, yellow or reddish brown.
2. Hydroxide	Weak base; light green in colour and easily oxidised.	Much weaker base exhibits amphoteric nature in giving ferrites.
3. Reducing or oxidising property.	Reducing agents, *e g.*, reduce $KMnO_4$, $K_2Cr_2O_7$. $HgCl_2$, $AgNO_3$ and $AuCl_3$.	Oxidising agents, *e.g.*, oxidize KI.
4. With nitric oxide	Give dark brown nitroso compounds, *e.g.* $FeSO_4$,NO.	No action.

16. **Ferrous Sulphate, Green Vitriol, $FeSO_4.7H_2O$** (हरा कसीस). Ferrous sulphate may be obtained by dissolving scrap iron in dilute sulphuric acid but in the laboratory it is generally obtained from the *Kipp's waste* which contains ferrous sulphate with free sulphuric acid.

The liquid is concentrated in the presence of scrap iron which reacts with excess of sulphuric acid to give ferrous sulphate, and the nascent hydrogen liberated reduces any ferric salt present to ferrous. On filtering and allowing to stand $FeSO_4.7H_2O$ crystallizes out. Ferrous sulphate containing 6, 5, 3, 2, 1 or no molecules of water of crystallization is also known.

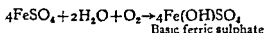
In commerce, ferrous sulphate is obtained by exposing big heaps of moist iron pyrites to air when slow oxidation takes place.



$$2FeS_2+2H_2O+7O_2 \rightarrow 2FeSO_4+2H_2SO_4$$

From the solution obtained crystals of ferrous sulphate are obtained as in the laboratory method.

Properties and Uses. (*i*) Light green crystals of ferrous sulphate lose water and turn brown on exposure to air, due to oxidation.



$$4FeSO_4+2H_2O+O_2 \rightarrow \underset{\text{Basic ferric sulphate}}{4Fe(OH)SO_4}$$

(*ii*) On heating it decomposes as follows :

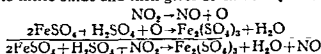


$$2FeSO_4 \rightarrow Fe_2O_3+SO_2+SO_3$$

(*iii*) With nitric oxide, ferrous sulphate turns black due to the formation of nitroso ferrous sulphate, $FeSO_4.NO$ (destroyed by heat).

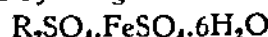
(*iv*) *Reducing property.* It is good reducing agent. For example, it decolorises acidified potassium permanganate and turns acidified potassium dichromate green.

Nitrogen dioxide, when passed through its solution, is first reduced to nitric oxide and then gives black $FeSO_4.NO$.



$$NO_2 \rightarrow NO+O$$
$$2FeSO_4+H_2SO_4+O \rightarrow Fe_2(SO_4)_3+H_2O$$
$$\overline{2FeSO_4+H_2SO_4+NO_2 \rightarrow Fe_2(SO_4)_3+H_2O+NO}$$

(*v*) It forms double salts with sulphates of alkali metals. These can be represented by the general formula :

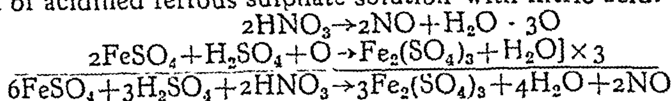


$$R_2SO_4.FeSO_4.6H_2O$$

(*vi*) With ammonium sulphate, it gives *ferrous ammonium sulphate* (Mohr's salt), $FeSO_4.(NH_4)_2SO_4.6H_2O$. This is not oxidized so readily as ferrous sulphate and is, therefore, used in volumetric analysis in preference to ferrous sulphate.

Ferrous sulphate is largely used in the manufacture of blue-black ink and as mordant in the dyeing and tanning industries. It is also used in the preparation of Mohr's salt, ferric oxide, ferric alum and nitric oxide.

17. **Ferric Sulphate, $Fe_2(SO_4)_3$.**—It is prepared by the oxidation of acidified ferrous sulphate solution with nitric acid.

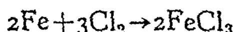


$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$
$$[2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$
$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

The yellowish brown solution on concentration deposits a whitish mass having the composition, $Fe_2(SO_4)_3.9H_2O$. The anhydrous salt may be obtained by heating the hydrate.

With sulphates of alkali metals, it gives double salts called *alums*, *e.g.*, iron alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3\ 24H_2O$, used in volumetric analysis.

18. **Ferric chloride $FeCl_3$.**—Anhydrous ferric chloride is prepared by passing dry chlorine over heated iron (Fig. 58·12) when the salt sublimes over as deep red crystalline plates.



$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

An aqueous solution of the salt is obtained by dissolving ferric hydroxide in dilute hydrochloric acid.

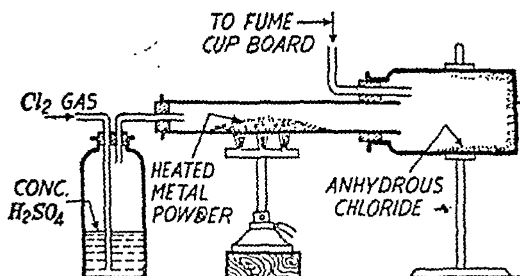
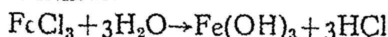


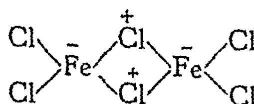
Fig. 58·12—Preparation of anhydrous ferric chloride

The anhydrous salt is deliquescent and soluble in water, alcohol and ether. The aqueous solution undergoes hydrolysis and reacts acidic towards litmus.



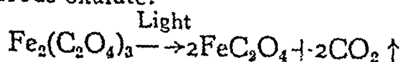
$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

Its vapour density corresponds to the formula Fe_2Cl_6 at 440°C and $FeCl_3$ at 750°C. Hydrates of ferric chloride containing 12, 7, 5 and 4 molecules of water of crystallization are known. It forms a number of double salts, *e.g.*, $2KCl.FeCl_3.H_2O$. Ferric chloride is most probably covalent and dimerized.



It is used as a reagent in the laboratory and in medicine.

19. **Blue Prints.**—Ferric salts, containing certain anions having reducing properties, *e.g.*, oxalate and citrate, are reduced to ferrous salts when exposed to light. This fact is made use of in making *blue prints*. For example, ferric oxalate on standing in light gives ferrous oxalate.



$$Fe_2(C_2O_4)_3 \xrightarrow{\text{Light}} 2FeC_2O_4 + 2CO_2 \uparrow$$

An ink drawing is obtained on a transparent paper. To get a blue print of the drawing, it is placed over a paper to which ferric oxalate or citrate solution has been applied and dried. On

[illegible] excepting [illegible] dipping the [illegible] ite gives a blue colour due to the formation of ferrous ferricyanide whereas ferric oxalate or ferric citrate gives only a brown substance which can be washed away. Thus white lines are obtained as there are in the ink drawing, on a deep blue ground. Thus a blue print of the original ink drawing is obtained.

In actual practice blue-print papers have a coating of a mixture of potassium ferricyanide and ammonium-ferric citrate and need only exposure and washing. In the laboratory, 100 ml. of a 10% potassium ferricyanide solution is mixed with 100 ml. of a 13% ammonium ferric citrate solution. For preparing blue-print papers, this mixture is filtered and applied evenly to one side of a tough, well-sized paper with the help of clean camel hair brush. It is dried and kept in dark room.

20. **Tests for Iron.**—(i) *Colour*. Ferrous salts are light green while ferric salts are yellow to reddish brown.

(ii) *Charcoal cavity test.* Iron compounds when heated on charcoal with sodium carbonate give reddish scales of the oxide.

(iii) *Borax bead test.* Iron salts impart a pale green colour to the borax bead in the reducing flame. In oxidizing flame, the colour is yellowish brown when hot and yellow when cold.

Distinguishing Tests between Ferrous and Ferric salts.

Test	Ferrous salts	Ferric salts
1. To the salt solution add NH_4OH.	Greenish white ppt. of $Fe(OH)_2$.	Reddish brown ppt of $Fe(OH)_3$.
2. Salt solution + potassium ferrocyanide solution.	A bluish white ppt. of ferrous ferricyanide first produced turns blue on exposure to air due to oxidation.	A dark blue ppt. of ferric ferrocyanide or Prussian blue $Fe_4[Fe(CN)_6]_3$ is obtained.
3. [illegible]	[illegible]	A reddish-brown coloration only is produced
4 To the salt solution add ammonium sulphocyanide.	No action.	A blood-red coloration obtained due to the formation of $Fe(CNS)_3$

21. **Estimation of Iron**—(*a*) **Gravimetric Method.** A known weight of the iron salt is heated with nitric acid to oxidize it to the ferric state if not so already. This is treated with ammonium hydroxide and the gelatinous ferric hydroxide thus precipitated is filtered, washed, dried and ignited. The weight of the ferric oxide left as residue is determined and therefrom the percentage of iron calculated.

(b) **Volumetric Method.** Concentration of a ferrous salt solution is determined by titrating it against a standard solution of potassium permanganate or potassium dichromate in the presence of dilute sulphuric acid. In the presence of chloride ions, titration is done against potassium dichromate.

Ferric salt is first reduced to ferrous salt with zinc and sulphuric acid or stannous chloride and then titrated.

TEST YOURSELF ON THESE REACTIONS

Write equations for the reactions, if any, between :

1. Ferric oxide+Carbon monoxide.
2. Manganous oxide+Silica.
3. Calcium oxide+Phosphorus pentaoxide.
4. Iron+(i) Oxygen (burning) ; (ii) Steam ; (iii) HCl ; (iv) Dil. H_2SO_4 ; (v) HNO_3 (dil. and concentrated) ; (vi) Chlorine.
5. Action of heat on (i) Ferrous oxalate ; (ii) Ferrous sulphate ; (iii) potassium ferrocyanide ; (iv) Nickel carbonyl ; (v) Cobalt nitrate.
6. Iron pyrites+Moisture+Air.
7. Ferrous sulphate+Water+Air.
8. Ferrous sulphate+(i) Nitrogen dioxide ; (ii) Nitric acid ; (iii) Nitric oxide.

QUESTIONS

1. How many of the following terms can you define or explain ?

Passivity	Haematite	Cast iron
Carbonyls	Magnetite	Wrought iron
Cementite	Pig iron	Alloy steels
Puddling	Hardening	Blast furnace
Annealing	Tempering	Cup and cone feeder
Nitriding	Case hardening	Bessemer converter
Hot short	Cold short	Green vitriol
Rusting	Spiegeleisen	Mohr's salt

2. Give the name of composition of the common ore of iron. Describe briefly the commercial method of extraction of iron, discussing the reactions which take place in the blast furnace. *(Delhi H.S. 1971, 69, 60 ; Delhi Pre-Medical 1960)*

3. What are important ores of Iron ? How is iron extracted ?

Or

Indicate the difference between Cast Iron, wrought iron and steel. How is steel prepared ? *(All India H.S. 1971)*

4. What are different forms of iron ? Summarize with the help of equations the reactions taking place in the blast furnace used in the metallurgy of iron. *(Punjab H.S. 1963)*

5. Give one method for the conversion of iron into steel. What is the difference in the composition and properties of (i) Cast iron, and (ii) Steel ?

How are the properties of iron altered on (i) heat treatment, and (ii) addition of other elements ?

6. What is steel ? Describe the Bessemer process for the manufacture of steel. Why is steel prepared by this method regarded inferior to steel obtained by the Open-Hearth method ? Upon what factors do the properties of steel depend ?

7. Describe giving neat diagram the manufacture of steel from cast iron. Discuss the statement, "The properties of steel depend on (a) its carbon content, (b) its final treatment, and (c) alloy elements." *(All India H.S. 1968, 67, 66 ; Punjab H.S. 1962, 61)*

8. Write short notes on :
(i) Rusting of iron. *(Punjab Pre-Univ. 1963)*
(ii) Passivity. *(Punjab H.S. 1963 ; Punjab Inter. 1960)*
(iii) Wrought iron. *(Delhi H.S. 1963)*

9. Give the preparation, properties and uses of :
(i) Ferrous sulphate.
(ii) Ferric alum.
(iii) *Ferric chloride.* *(Delhi H.S. 1971 ; Punjab Pre-University 1963)*

NEW TYPE TEST PAPER III

(Based on Chapters 51—58)

Completion Test

1. Fill in the blanks with a correct word or words in the following statements :

(i) Sodium is prepared on a commercial scale by the electrolysis of......or......

(ii) In the causticizing process, caustic soda is manufactured by boiling .....with .....when......is formed and......is precipitated.

(iii) Calcium burns in air forming......and a little......

(iv) Calcium combines with hydrogen to give......of the formula......

(v) On adding water to quicklime, it is converted to......

(vi) Lime mortar is a mixture of......and...

(vii) The raw material needed in the manufacture of Portland cement are 1..... , 2......, and 3......

(viii) On heating......(a soluble calcium compound) is converted into......(an insoluble calcium compound).

True-False Test

2. In the following statements mark T before true statement and F before false ones. Supply the word or words which must be substituted for the italicised words in false statements.

(i) Because of their great reactivity, sodium and potassium are always found in the *free* state in nature.

(ii) Sodium is a *good* conductor of *electricity.*

(iii) Sodium amalgam is used as an *oxidising agent.*

(iv) Crystals of washing soda, on standing in air, *lose* water.

(v) Potassium resembles sodium but is *less* reactive chemically.

(vi) Magnesium continues to burn in an atmosphere of *steam.*

(vii) Magnesium *sulphate* is used as a purgative.

(viii) Calcium *oxide* is used for drying gases.

(ix) Glass is a *solid solution* of sodium and potassium silicates.

Selection Test

3. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(i) Sodium burns in excess of air to give (*a*) sodium oxide, (*b*) sodium peroxide, (*c*) sodium hydroxide.

(ii) When sodium hydroxide is dissolved in water, the solution (*a*) becomes hot, (b) becomes cold, (c) remains at the original temperature.

(*iii*) Caustic soda does not react with (*a*) aluminium, (*b*) tin, (*c*) silicon, (*d*) magnesium.

(*iv*) The formula of crystalline sodium carbonate is (*a*) $Na_2CO_3.H_2O$, (*b*) $Na_2CO_3.5H_2O$, (*c*) $Na_2CO_3.10H_2O$.

(*v*) Ceramics deal with the manufacture of (*a*) glass, (*b*) pottery, (*c*) cement.

(*vi*) Our bones and teeth are made of (*a*) calcium phosphate, calcium carbonate, (*c*) calcium silicate.

Matching Test

4. Mark each item in list II with appropriate numbers—(*i*), (*ii*), (*iii*), etc., so that it becomes related with the corresponding items in list I.

List I	List II
(*i*) Nelson cell	(...) Slow cooling of glass.
(*ii*) Caster-Kellner cell	(..) Porous diaphragm cell.
(*iii*) Caliche	(...) $CaSO_4.2H_2O$.
(*iv*) Epsom salt	(...) Crude sodium nitrate.
(*v*) Clinker	(...) $2CaSO_4.H_2O$.
(*vi*) Gypsum	(...) Mercury diaphragm cell.
(*vii*) Plaster of Paris	(...) $MgSO_4.7H_2O$.
(*viii*) The batch	(...) Pea-size particles obtained by heating a mixture of powdered limestone and clay.
(*ix*) Cullet	(...) Broken pieces of glass.
(*x*) Annealing	(...) Mixture of sand, limestone, and washing soda.

Multiple-Choice Test

5. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) Sodium nitrate is not used in gun-powder because it is (*a*) hygroscopic, (*b*) very soluble in water, (*c*) amorphous.

(*ii*) The mineral containing magnesium carbonate mixed with calcium carbonate is (*a*) magnesite, (*b*) dolomite, (*c*) carnallite.

(*iii*) Calcium metal tarnishes in air due to the formation of (*a*) calcium oxide, (*b*) calcium hydroxide, (*c*) calcium carbonate.

(*iv*) Plaster of Paris is (*a*) $CaSO_4.2H_2O$, (*b*) $2CaSO_4.H_2O$, (*c*) $CaSO_4$, (*d*) $CaSO_4.8H_2O$.

(*v*) Glass is (*a*) a definite chemical compound, (*b*) an element, (*c*) a solid solution.

(*vi*) Broken glass pieces used in the manufacture of glass are called (*a*) batch, (*b*) raw material, (*c*) cullet.

(*vii*) Glass articles if cooled suddenly become (*a*) transparent, (*b*) opaque, (*c*) brittle.

(*viii*) Colouring materials used in glass industry are (*a*) metallic oxides, (*b*) oxides of non-metals, (*c*) synthetic dyes.

Completion Test

6. Fill in the blanks with a correct word or words in the following statements :

(*i*) In Froth flotation process, the powdered ore is added to ......and a little .....and agitated by means of......

(*ii*) Volatile metals are generally refined by......

(*iii*) Roasted iron ore is mixed with coke and limestone and smelted in a......furnace with a......arrangement at the top.

(*iv*) Spiegeleisen is an alloy of iron,......and......

(*v*) When concentrated ore (mainly silver sulphide) is treated with sodium cyanide solution, silver forms......from which it is precipitated by treating it with......

(*vi*) Silver can be separated from a zinc-silver alloy by......

(*vii*) After developing the photograpic film, it is fixed by treating it with......solution.

(*viii*) Thermit is a mixture of .....and......

(*ix*) The principal ore of lead is......of the formula......

(*x*) Blister copper is refined either by. .. or by......

7. Fill in the blanks with a correct word or words in the following statements :

(*i*) Important ore of copper is ... .having the formula...... It is found in India at......in.... .State.

(*ii*) Matte is the molten mass containing mainly... .with a little......

(*iii*) Brass contains . .. % of.. . and... . % of .....

(*iv*) The chief ore of aluminium is. . and in India it is found in......, ... and....

(*v*) Principal ore of mercury is..... , having the formula......

(*vi*) ......or mercuric chloride is a dangerous poison. Its antidote being......

(*vii*) ....or mercurous chloride is used in *medicine* as......

True-False Test

8. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicised words in the false statements.

(*i*) *Cast iron* is the purest form of iron.

(*ii*) Iron is *insoluble* in fuming nitric acid.

(*iii*) Ferrous sulphate is a *reducing agent*.

(*iv*) In the electrolytic refining of metals the *cathode* is made of a sheet of the pure metal.

(*v*) Silver is *more soluble* in molten zinc than in molten lead.

(*vi*) Molten zinc and lead are *miscible*.

(*vii*) Mercurous chloride is a *white crystalline* compound.

(*viii*) Tin *exhibits variable* valency.

(*ix*) *Lead carbonate* is used as a white paint.

Multiple-Choice Test

9. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) The percentage of carbon is least in (*a*) cast iron, (*b*) wrought iron, (*c*) steel.

(*ii*) Copper does not displace (*a*) silver, (*b*) gold, (*c*) zinc from the solution of its salt.

(*iii*) The oxide and carbonate ores of copper are concentrated by (*a*) Gravity process, (*b*) Froth flotation process, (*c*) Electromagnetic separation.

(*iv*) Copper pyrites are concentrated by (*a*) Gravity process, (*b*) Froth flotation process, (*c*) Electromagnetic separation.

(*v*) On heating silver nitrate (*a*) Silver nitrite, (*b*) Metallic silver, (*c*) Silver oxide is formed.

(*vi*) A developer used in photography is (*a*) a reducing agent, (*b*) an oxidising agent, (*c*) a weak acid.

(*vii*) The amorphous allotropic modification of tin is (*a*) rhombic, (*b*) tetragonal, (*c*) grey tin.

Matching Test

10. Mark each item in list II with appropriate numbers (*i*), (*ii*), (*iii*), etc. so that it becomes related with the corresponding items in list I.

List I	List II
(*i*) Malleability	(...) Weight that can be supported by wire of 1 sq. inch cross-section.
(*ii*) Annealing	(...) Heating steel in contact with charcoal and quenching in oil.
(*iii*) Hardening	(...) Heating steel to bright red heat and then cooling it slowly.
(*iv*) Tempering	(...) Heating steel to bright redness and then cooling suddenly in oil or water.
(*v*) Ductility	(...) Earthy particles, *e.g.*, sand, limestone, etc., present in the ore.
(*vi*) Tenacity	(...) Property of being drawn into wires.

(*vii*) Gangue	(...) Substance used in metallurgy to remove silica, etc.
(*viii*) Flux	(...) Property of being drawn into sheets.
(*ix*) Slag	(...) Heating the ore strongly in absence of air.
(*x*) Smelting	(...) Stirring the molten metal with logs of green wood.
(*xi*) Roasting	(...) Fusible compound of impurities.
(*xii*) Calcination	(...) Heating the ore strongly in excess of air.
(*xiii*) Poling	(..) Reduction of the roasted or calcined ore.
(*viv*) Weathering	(..) Rusting or tarnshing of metals.
(*xv*) Case hardening	(...) Heating hard steel below redness and cooling slowly.

Selection Test

11. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) Principal ore of tin is ..... The miners speak of it as (*a*) black tin, (*b*) white tin, (*c*) block tin.

(*ii*) The metal used in storage batteries is (*a*) iron, (*b*) copper, (*c*) tin, (*d*) lead.

(*iii*) The mixture of aluminium powder and ammonium nitrate is called (*a*) thermit, (*b*) ammonal, duralumin.

(*iv*) Red bauxite cannot be purified by (*a*) Baeyer's process, (*b*) Hall's process, (*c*) Serpek's process.

(*v*) Process of covering the kitchen utensils with a thin layer of tin is called (*a*) tinplating, (*b*) tinning, (*c*) alloy formation

Completion Test

12. Fill in the blanks with a correct word or words in the following statements :

(*i*) When a carbonate is treated with dil. HCl . is observed.

(*ii*) When a sulphide is warmed with dil. H_2SO_4 . . gas is evolved. It has a smell like that of . and turns . . paper black.

(*iii*) On warming a sulphite with dil. H_2SO_4 . gas is evolved. It has a smell like that of. . and turns .. paper green.

(*iv*) An intense blue colour with diphenylamine shows the presence of . ...

(*v*) The precipitate of lead sulphate is soluble in......

(*vi*) The precipitate of......turns black on addition of ammonium hydroxide.

(*vii*) The solution of ferric chloride gives a......colour on addition of potassium sulphocyanide.

(*viii*) When Nessler's solution is added to a solution of ammonium salt, a......is formed.

(*ix*) Milkiness, which sometimes appears on passing H_2S in second group, is due to the......

(*x*) A lacquer is a solution of......and......in some solvent.

Selection Test

13. In the following statements put √ mark on the most suitable word or expression out of the various possible alternatives suggested therein :

(*i*) The colour of the ppt. obtained on adding $K_4Fe(CO)_6$ to a zinc salt solution, is (*a*) bluish white, (*b*) blue, (*c*) chocolate brown.

(*ii*) Precipitate of (*a*) lead chloride, (*b*) silver chloride, (*c*) mercurous chloride is soluble in hot water.

(*iii*) Precipitate of silver chloride is soluble in (*a*) nitric acid, (*b*) ammonia hydroxide, (*c*) aqua regia.

(*iv*) Ammonium chloride is added in the third group to (*a*) precipitate iron and aluminium, (*b*) prevent the precipitation of the redicals of 1st and 2nd groups, (*c*) to prevent the precipitation of the radicals of 4th, 5th and 6th groups

(*v*) Precipitate of tin sulphide is soluble in (*a*) yellow ammonium sulphide, (*b*) ammonium hydroxide, (*c*) dilute hydrochloric acid.

(*vi*) Reddish brown vapours of (*a*) Nitrogen dioxide, (*b*) Bromine turn ferrous sulphate solution black.

(*vii*) Violet colour imparted to flame by potassium salts (*a*) is visible, (*b*) is invisible, (*c*) appears pink, (*d*) appears green through blue glass.

(*viii*) The residue on charcoal cavity is brown when hot and yellow when cold indicates (*a*) lead, (*b*) tin, (*c*) zinc.

(*ix*) Borax bead test is employed for (*a*) colourless salts, (*b*) coloured salts (*c*) volatile salts.

True-False Test

14. In the following statements mark T before true statements and F before false ones. Supply the word or words which must be substituted for the italicized words in the false statements.

(i) *Mn* and *Zn* belong to the III group of Qualitative Analysis.

(*ii*) *Magnesium* gives a green colour in cobalt nitrate charcoal cavity test.

(*iii*) In the borax bead test, copper gives a *bluish green* colour in the oxidising flame and a *red* colour in the reducing flame.

(*iv*) If the salt gives no action with dilute hydrochloric acid, we infer that *carbonate, bicarbonate, sulphide, sulphite, thiosulphate* and *nitrite* are absent.

(*v*) A *sulphite* gives a violet colour with sodium nitroprusside solution.

(*vi*) When a salt is treated with chlorine water and carbon disulphide, a violet colour in the lower carbon disulphide layer indicates a *bromide.*

(*vii*) If a salt gives with potassium iodide a yellow precipitate which is soluble in hot water, it must be mercurous.

(*viii*) If the given salt is insoluble in water, it indicates the absence of *sodium, potassium* and *ammonium*.

Some Examination Questions

15. Indicate which of the following statements are not correct :

(*a*) An ion carries an electric charge.

(*b*) Ions are nascent atoms.

(*c*) Ions are present in solutions only.

(*d*) All ions are coloured.

(*e*) Davy was responsible for the periodic classification of elements.

(*f*) Chlorine is good for digestion.

(*g*) Ozone is present near open drains. (Delhi H.S. [illegible])

16. Fill in the blanks to make the following statements complete and correct :

(*i*) A decinormal solution of sodium [illegible] .... gm. of an anhydrous salt in .... c.c. solution. [illegible] with sulphuric acid, the correct indicator is.

(*ii*) The dust-free atmospheric air contains [illegible] ......per cent of..... and......per cent of [illegible] following ......

(*iii*) One gm. equivalent of oxygen at N.T.P. [illegible] volume of......

(*iv*) Brass contains the following elements [illegible] .. ...Duralumin is an alloy of .....

(*v*) Ozone is an .....form of oxygen. ([illegible] H.S. [illegible])

17. Correct the following statements

(*i*) Water is a mixture of hydrogen and oxygen.

(*ii*) Phosphorus is a chemical compound.

(*iii*) The horizontal rows in the Periodic Table are called groups.

(*iv*) Hard water freely lathers with soap.

(*v*) The covalent compounds are ionised in solution.

(Delhi H.S. [illegible])

18. Which of the following statements are correct and which are not correct ? Give one reason in each case in support of your answer.

(*a*) A solution of sodium carbonate has no action on litmus paper.

(*b*) Bronze is a compound of copper and silver.

(c) Sodium occurs free in nature.

(*d*) Atomic weight is the basis of the modern periodic classification of elements.

(*e*) White lead paint remains uneffected in a chemical laboratory.

(*f*) Aluminium vessels can be used for concentrating sodium hydroxide solution.

(*g*) Ions do not carry any electric charge.

(*h*) A solution of copper sulphate has no action on litmus paper.

(*i*) Zinc carbonate is obtained by adding sodium carbonate to zinc sulphate solution.

(*j*) Air is a mixture. (*Delhi H.S. 1971*)

19. State, giving reasons, whether the following statements are correct or wrong :

(*i*) A solution of ferric sulphate in water has no action on litmus paper.

(*ii*) Ions are the same as atoms.

(*iii*) Sodium occurs free in nature.

(*iv*) The modern periodic table is based on atomic weights of elements.

(*v*) Aluminium is obtained from its oxide by heating with coke.

(*vi*) A mixture of zinc and silver can be separated by the process of distillation.

(*vii*) Bronze is an alloy of zinc and aluminium.

(*viii*) Red lead paint will remain unaffected in a chemical laboratory.

(*ix*) Zinc pans can be used for concentrating caustic soda-solutions. (*Delhi H.S. 1970*)

20. Correct the following statements :

(*i*) Borax solution is neither alkaline nor acidic.

(*ii*) Chlorine reacts with hot sodium hydroxide solution to give hydrochloric acid and water.

(*iii*) The order of increasing reactivity of halogen is :

Bromine, chlorine, Iodine.

(*iv*) Nitrogen and hydrogen combine in sunlight at ordinary temperature and pressure.

(*v*) Hydrogen peroxide can be distinguished from ozone by formation of orange colour with chloroform. (*Delhi H.S. 1970*)

KEY TO SOLUTIONS

1. (*i*) Fused caustic soda, fused sodium chloride, (*ii*) wash- [illegible]

bicarbonate, calcium carbonate.

2. (*i*) F—combined, (*ii*) T, (*iii*) F—reducing agent, (*iv*) T, (*v*) F—more, (*vi*) T, (*vii*) T, (*viii*) T, (*ix*) T.

3. (*i*) *b*, (*ii*) *a*, (*iii*) *d*, (*iv*) *c*, (*v*) *b*, (*vi*) *a*.

4. (*x*), (*i*), (*vi*), (*iii*), (*vii*), (*ii*), (*iv*), (*v*), (*ix*), (*viii*).

5. (*i*) *a* ; (*ii*) *b* ; (*iii*) *c* ; (*iv*) *b* ; (*v*) *c* ; (*vi*) *c* ; (*vii*) *c* ; (*viii*) *a*.

6. (*i*) Water, pine oil, compressed air, (*ii*) distillation, (*iii*) [illegible] ...on, (*v*) sodium argentocy- [illegible] (*viii*) ferric oxide, alu- [illegible] ing, electrolytic refining.

7. (*i*) Copper pyrites ; $CuFeS_2$; Singbhum ; Bihar.

(*ii*) Cuprous sulphide ; ferrous sulphide.

(*iii*) 67 ; Copper 33 ; Zinc.

(*iv*) Bauxite ; Kashmir ; Bihar ; Bombay.

(*v*) Cinnabar ; HgS.

(*vi*) Corrosive sublimate ; white of an egg.

(*vii*) Calomel ; purgative.

8. (*i*) F—wrought iron, (*ii*) T, (*iii*) T, (*iv*) T, (*v*) T, (*vi*) F—immiscible, (*vii*) F—white amorphous, (*viii*) T, (*ix*) F—basic lead carbonate.

9. (*i*) *b*, (*ii*) *c*, (*iii*) *a*, (*iv*) *b*, (*v*) *b*, (*vi*) *a*, (*vii*) *c*.

10. (*vi*), (*xv*), (*ii*), (*iii*), (*vii*)(*v*), (*viii*), (*i*), (*xii*), (*xiii*), (*ix*), (*xi*), (*x*), (*xiv*), (*iv*).

11. (*i*) tinstone—*a* ; (*ii*) *d* ; (*iii*) *b* ; (*iv*) *c* ; (*v*) *b*.

12. [illegible]

eggs, [illegible]

dichr[illegible]

mercurous chloride, (*vii*) blood red, (*viii*) brown precipitate, (*ix*) colloidal sulphur, (*x*) cellulose nitrate or acetate, synthetic resin, organic.

13. (*i*) *a* ; (*ii*) *a* ; (*iii*) *b* ; (*iv*) *c* ; (*v*) *a* ; (*vi*) *a* ; (*vii*) *c* ; (*viii*) *a* ; (*ix*) *b*.

14. (*i*) F—Fe, Cr, Al ; (*ii*) F—zinc ; (*iii*) T ; (*iv*) T ; (*v*) F—sulphide ; (*vi*) F—iodide ; (*vii*) F—lead ; (*viii*) T.

15. (*b*), (*d*), (*e*), (*f*), (*g*).

FIC—7·72—27

16. (*i*) 53 ; 1000 ; Methyl orange.

(*ii*) 78·03 ; Nitrogen 20·29 ; Oxygen, Carbon dioxide, Water vapours, Noble gases, H_2S, SO_2, NH_3, O_3 and oxides of nitrogen.

(*iii*) 5·6 litres.

(*iv*) Copper and zinc ; Utensils, condenser tubes, sheets and cartridges, Aluminium, Copper, manganese and magnesium.

(*v*) Allotropic.

17. (*i*) Water is a compound of hydrogen and oxygen.

(*ii*) Phosphorus is an element.

(*iii*) The horizontal rows in the Periodic Table are called periods.

(*iv*) Hard water does not lather with soap.

(*v*) The covalent compounds are not ionized in solution.

Appendix I

NOMENCLATURE OF INORGANIC COMPOUNDS

The International Union of Pure and Applied Chemists published rules for the systematic naming of inorganic compounds in 1957. The system of nomenclature recommended by them is known as the I.U.P.A.C. system of nomenclature and is widely accepted. *Details of this system of nomenclature are as follows :*

1. **Binary Compounds.**—In naming a binary compound the more electropositive element is named first and is followed by the name of the other element with its last part replaced by the suffix *ide*. For example,

AlN	Aluminium nitride
BaO	Barium oxide
BF_3	Boron fluoride
CaC_2	Calcium carbide
Mg_3B_2	Magnesium boride
OF_2	*Oxygen fluoride.*

In addition to these binary compounds some other compounds containing more than two elements are also named like binary compounds. Some examples of such compounds are given below :

$Ba(N_3)_2$	Barium azide
$CaCN_2$	Calcium cyanamide
$NaNH_2$	Sodium amide

Binary compounds containing hydrogen also follow the same rules. For example,

HBr	*Hydrogen bromide*
CaH_2	Calcium hydride

Trivial names are, however, used in the case of quite a large number of binary compounds of hydrogen. For example,

NH_3	Ammonia	CH_4	Methane
AsH_3	Arsine	C_2H_6	Ethane
PH_3	Phosphine	SiH_4	Silane
SbH_3	Stibine	GeH_4	Germane

Those binary compounds of hydrogen which act as acids in their aqueous solution, are named as *hydro......ic* acid, while names of their salts end in *ide*. For example,

Formula of the acid	*Name of the acid*	*Salts named as*
HCl	*Hydro*chlor*ic* acid	Chlor*ides*
HCN	*Hydro*cyan*ic* acid	Cyan*ides*
H_2S	*Hydro*sulphur*ic* acid	Sulph*ides*
HBr	*Hydro*brom*ic* acid	Brom*ides*

2. **Valency State.**—When an element shows variable valency and forms two series of salts these are distinguished by adding *ous* and *ic* at the end of the name of the element concerned. For example, in the salts of iron, mercury and tin—

$FeCl_2$	Ferrous chloride
$FeCl_3$	Ferric chloride
Hg_2Cl_2	Mercurous chloride
$HgCl_2$	Mercuric chloride
$SnCl_2$	Stannous chloride
$SnCl_4$	Stannic chloride

The termination *ous* and *ic* are, however, satisfactory only where the element does not show more than two valency states.

To overcome the above limitation, Stock suggested in 1919 the use of a Roman numeral in parentheses indicating the valency state of the atom. Examples of some compounds named according to Stock's suggestion are :

FeO	Iron (II) oxide
Fe_2O_3	Iron (III) oxide
Fe_3O_4	Iron (II, III) oxide
$PbCl_2$	Lead (II) chloride
$PbCl_4$	Lead (IV) chloride

Stock system of nomenclature is also being used for naming some ternary compounds such as

$Cr(CH_3COO)_2$	Chromium (II) acetate
NiCN	Nickel (I) cyanide

In a number of cases a compound cannot be named unambiguously according to the above system. For example :

(*i*) Both NO_2 and N_2O_4 would be named nitrogen (IV) oxide.

(*ii*) $Pb_2O_3(PbO.PbO_2)$ and $Pb_3O_4(2PbO.PbO_2)$ both will be named Lead (II, IV) oxide.

The Stock system of nomenclature does not work in the cas of some compounds in which the valency state of the elements i uncertain, *e.g.*, N_2O, NO. In naming such compounds the use o Greek numeral prefixes mono, di, tri, etc. is preferred. In un equivocal cases the prefix mono is generally omitted. Som examples of names using Greek numerals are :

NO	Nitrogen oxide
NO_2	Nitrogen dioxide
N_2O_4	Dinitrogen tetroxide
Pb_2O_3	Dilead trioxide
Pb_3O_4	Trilead tetroxide

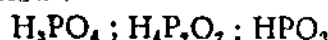
3. **Oxy-acids.**—Generally an element forms two oxy-acids The name of the acid with lower proportion of oxygen ends in *ou* while that of the other with higher proportion of oxygen ends in *ic* Their salts are named ending with *ites* and *ates* respectively. Fo example, in the case of acids of nitrogen and sulphur.

Formula of the acid	*Name of the acid*	*Salts named as*
HNO_2	Nitr*ous* acid	Nitr*ites*
HNO_3	Nitr*ic* acid	Nitr*ates*
H_2SO_3	Sulphur*ous* acid	Sulph*ites*
H_2SO_4	Sulphur*ic* acid	Sulph*ates*

In case an element gives more than two acids, these are indicated as *hypo—ous* and *per—ic* acids while their salts are named as *hypo—ites* and *per—ates*. Thus in the case of four oxy acids of chlorine—

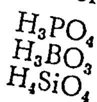
Formula of the acid	*Name of the acid*	*Salts named as*
HClO	*Hypo*chlor*ous* acid	*Hypo*chlor*ites*
$HClO_2$	Chlor*ous* acid	Chlor*ites*
$HClO_3$	Chlor*ous* acid	Chlor*ates*
$HClO_4$	*Per*chlor*ic* acid	*Per*chlor*ates*

Ortho-, Pyro-, and Meta-acids. In some cases a non-metallic element in the same oxidation state yields more than one oxy-acids. For example, phosphorus in its +5 oxidation state gives three oxy-acids as below :



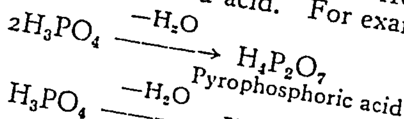
$$H_3PO_4 \; ; \; H_4P_2O_7 \; ; \; HPO_3$$

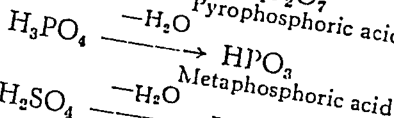
A group of such acids is distinguished by the use of prefixes *ortho, pyro and meta*. The prefix *ortho* is used for the most hydroxylated acid. For example,

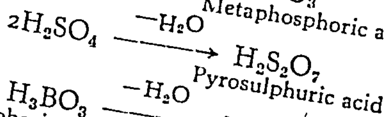


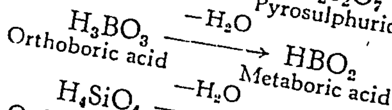
Orthosphosphoric acid
Orthoboric acid
Orthosilicic acid

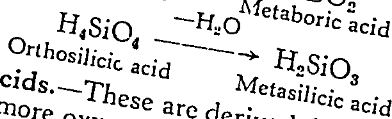
The oxy-acid, formed when two molecules of the ortho-acid lose one molecule of water, is termed *pyro*-acid while the one formed by the removal of one molecule of water from one molecule of the ortho-acid is termed the *meta*-acid. For example,







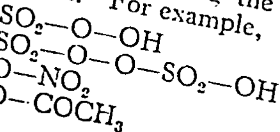




4. **Thio-acids.**—These are derived from oxy-acids by replace[ment] of one or more oxygen atoms by sulphur atoms. The acids a[nd] as their salts are named just like oxy-acids and their salts, with [the p]refix *thio*. For example,

Oxy-acid	*Thio-acid*	*Salts named as*
H_2SO_4 [Su]lphuric acid	$H_2S_2O_3$ Thiosulphuric acid	Thiosulphates
HNCO [Cya]nic acid	HNCS Thiocyanic acid	Thiocyanates
H_2CO_3 [Carb]onic acid	H_2CS_3 Trithiocarbonic acid	Trithiocarbonates
[O]=$P(OH)_3$ [Phos]phoric acid	S=$P(OH)_3$ Monothiophosphoric acid	Monothiophosphates

[5.] **Peroxy Acids.**—Acids obtained by replacement of one [oxy]gen atoms by —O—O— groups are called peroxy acids. [They are] named by adding the word *peroxy* before the name [of the pare]nt acid. For example,



Peroxymonosulphuric acid
Peroxydisulphuric acid
Peroxy nitric acid
Peroxy acetic acid

6. Hydrates and other Addition Compounds.—Salts [illegible] crystallization are called [illegible] with ammonia are called [illegible] ed as peroxyhydrates. In naming these compounds the number of added molecules is indicated by an Arabic number. A Greek prefix is also allowed but not preferred. A few names of such compounds are given below :

$BaCl_2.2H_2O$	Barium chloride-2-hydrate
$CuSO_4.5H_2O$	Copper (II) sulphate-5-hydrate
$CaCl_2.6NH_3$	Calcium chloride-6-ammoniate
$NaO-OH\ H_2O_2$	Sodium hydrogen peroxide-I-peroxyhydrate.

QUESTIONS

1. Give I U.P.A.C. names for the following compounds :

(i) NO_2, (ii) N_2O_4, (iii) $CuSO_4.5H_2O$, (iv) $FeCl_2$, (v) $FeCl_3$, (vi) $HO-O-NO_2$, (vii) $Cu(NH_3)_4SO_4$, (viii) $Cr(CH_3COO)_3$, (ix) H_2CS_3, (x) $H_4P_2O_7$, (xi) $HO.SO_2.O.OH$.

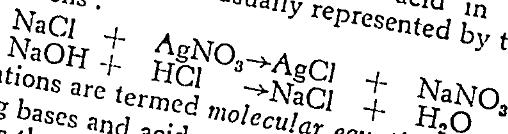
2. Write names of the compounds whose formulae are given below :

$CaCN_2$	PH_3	$HClO_4$
$Ba(N_3)_2$	GeH_4	$FeSO_4.7H_2O$
$NaNH_2$	Pb_3O_4	$HO.O.COCH_3$

Appendix II

IONIC EQUATIONS

1. **Molecular and Ionic Equations.**—On adding silver nitrate solution to a sodium chloride solution we get a white precipitate of silver chloride. Sodium chloride (a salt) is produced on mixing sodium hydroxide and hydrochloric acid in equivalent proportion. These reactions are usually represented by the following chemical equations:



$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$
$$NaOH + HCl \rightarrow NaCl + H_2O$$

These equations are termed *molecular equations*.

If all strong bases and acids and most salts are completely ionized, it follows that molecular equations given above are not strictly appropriate when no molecules are actually present. Chemists differ somewhat in their views on writing such equations. Some argue that since it is simpler to write molecular equations, there is no harm in writing such equations in the molecular form as long as the chemist is fully aware of the ionic character of the reacting substances. Others insist on expressing highly ionized compounds only in the form of ionic symbols which is obviously more exact. It is of course essential to know the ionic or no ionic nature of the compounds in advance.

A few simple rules needed for writing ionic equations ar given below:

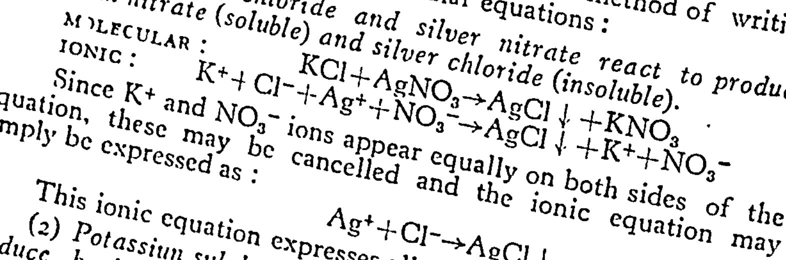
(*i*) All *strong electrolytes* are expressed in ionic symbols i they are soluble in water and all *weak electrolytes* and *covalent substances* are expressed in the molecular form.

(*ii*) Any electrolyte which is highly insoluble in water is generally written in the molecular form to indicate its insolubility. Actually, this is incorrect since many such solids are ionic in crystal form as well. This is, however, traditional.

(*iii*) In addition to the atoms which must balance on both sides of the equation, the ionic charges must also balance.

The following examples will illustrate the method of writing ionic equations for the given molecular equations:

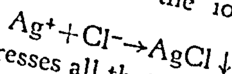
(1) *Potassium chloride and silver nitrate react to produce potassium nitrate (soluble) and silver chloride (insoluble).*



MOLECULAR: $KCl + AgNO_3 \rightarrow AgCl\downarrow + KNO_3$

IONIC: $K^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl\downarrow + K^+ + NO_3^-$

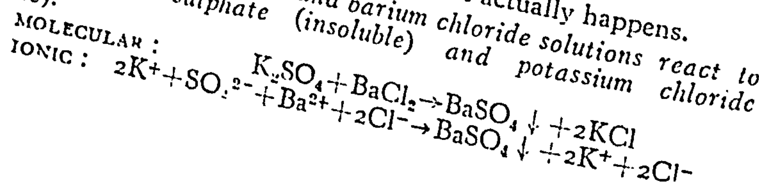
Since K^+ and NO_3^- ions appear equally on both sides of the quation, these may be cancelled and the ionic equation may mply be expressed as:



$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

This ionic equation expresses all that actually happens.

(2) *Potassium sulphate and barium chloride solutions react to duce barium sulphate (insoluble) and potassium chloride uble).*



MOLECULAR: $K_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2KCl$

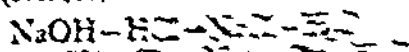
IONIC: $2K^+ + SO_4^{2-} + Ba^{2+} + 2Cl^- \rightarrow BaSO_4\downarrow + 2K^+ + 2Cl^-$

Cancelling the ions common to both sides :

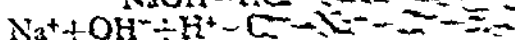


(3) *Sodium hydroxide and hyd[illegible] to produce sodium chloride (soluble) and [illegible]*

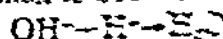
MOLECULAR :



IONIC :



Cancelling the ions common to both sides :



2. **The Ion-Electron Method for [illegible] for Oxidation-Reduction or Redox Re[illegible] Half-reactions).**—In this method the reaction is [illegible] half-reactions. In one half-reaction the [illegible] electrons and gets reduced and in the other [illegible] dized by supplying electrons. The two half-[illegible] separately and added in such a way that the [illegible] of one and on the right of the other cancel [illegible]

This procedure seems to imply that [illegible] redox reaction and travel through the [illegible] agent to the other species which is reduced [illegible] should, therefore, view the two half-[illegible] for obtaining the final answer rather than [illegible] reaction.

Different steps involved in writing a [illegible] the ion-electron method are :

(1) Separate the oxidising and the reducing agents.

(2) Write down one half equation for the [illegible] changing into its oxidized form.

(3) Write down the other half equation [illegible] agent changing into its oxidized form.

(4) Balance the atoms other than H and O for each half-reaction by adjusting coefficients, if necessary.

(5) Balance the oxygen atoms on the two sides by adding H_2O to the side deficient in oxygen.

(6) Balance the hydrogen atoms on the two sides by adding H^+ to the side deficient in hydrogen.

(7) Equalize the charge on both sides by adding electrons (e^-) to the side difficient in negative charge.

(8) If the reaction proceeds in basic solution, add enough OH^- on both sides of the half-reaction to get rid of H^+ appearing there. Combine H^+ and OH^- to give H_2O and remove H_2O duplication.

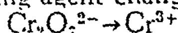
(9) Add these two balanced half-reactions in such a way that the electrons appearing on the right of one half-reaction and on the left of the other cancel. For this each half-reaction will be multiplied by some appropriate number before addition.

The following examples will illustrate the method :

Example 1. *Write balanced equation for the oxidation of ferrous to ferric ion by dichromate ion in acid solution.* The dichromate ion under these conditions yields Cr^{3+}.

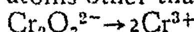
FOR ONE HALF-REACTION

(i) Writing down the reactant and product of the half-reaction for the oxidizing agent changing into its reduced form :



$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

(ii) Balancing the atoms other than oxygen :



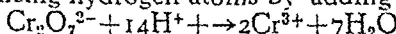
$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$

(iii) Balancing oxxygen atoms by adding $7H_2O$ on the right :



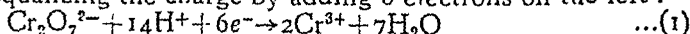
$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

(iv) Balancing hydrogen atoms by adding $14H^+$ on the left :



$$Cr_2O_7^{2-} + 14H^+ + \rightarrow 2Cr^{3+} + 7H_2O$$

(v) Equalizing the charge by adding 6 electrons on the left :



$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad ...(1)$$

FOR THE OTHER HALF-REACTIONS

(i) Writing down the reactant and product of the half-reaction for the reducing agent changing into its oxidized form :



$$Fe^{2+} \rightarrow Fe^{3+}$$

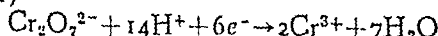
(ii) Equalizing the charge by adding one electron on the right :



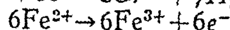
$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad ...(2)$$

ADDING TWO HALF-REACTIONS

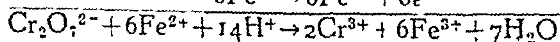
Multiplying the half-reaction (2) by 6 and adding to the half-reaction (1)



$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

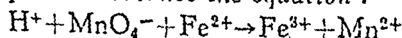


$$6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$$



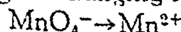
$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Example 2. *Balance the equation :*



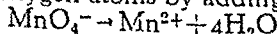
$$H^+ + MnO_4^- + Fe^{2+} \rightarrow Fe^{3+} + Mn^{2+}$$

(i) Writing down the reactant and product of the half-reaction for the oxidizing agent changing into its reduced form :



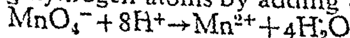
$$MnO_4^- \rightarrow Mn^{2+}$$

(ii) Balancing the oxygen atoms by adding $4H_2O$ on the right :



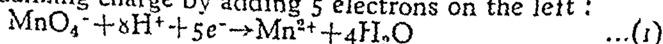
$$MnO_4^- \rightarrow Mn^{2+} + 4H_2O$$

(iii) Balancing hydrogen atoms by adding $8H^+$ on the left :



$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

(iv) Equalizing charge by adding 5 electrons on the left :



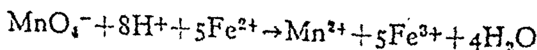
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad ...(1)$$

Writing in a similar manner the half-reaction for the reducing agent changing into an oxidized form :



$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad ...(2)$$

Multiplying half-reaction (2) by 5 and adding up to (1), we obtain :



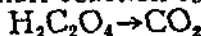
$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Example 3. *Balance the equation*

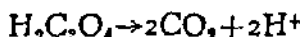

$$H_2C_2O_4 + H_2O_2 \rightarrow CO_2 + H_2O$$

(*a*) In this reaction oxalic acid is being oxidized to CO_2 and H_2O_2 is being reduced to H_2O.

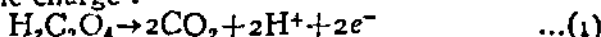
(*b*) (*i*) Writing half-reaction for the oxidation of oxalic acid :


$$H_2C_2O_4 \rightarrow CO_2$$

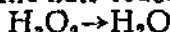
(*ii*) Balancing the atoms in the order carbon—Oxygen—ydrogen :


$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+$$

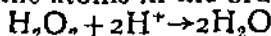
(*iii*) Equalizing the charge :


$$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^- \quad ...(1)$$

(*c*) (*i*) Next writing the half-reaction for the reduction of H_2O_2 :


$$H_2O_2 \rightarrow H_2O$$

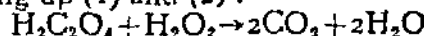
(*ii*) *Balancing the atoms in the order oxygen—hydrogen :*


$$H_2O_2 + 2H^+ \rightarrow 2H_2O$$

(*iii*) Equalizing the charge :


$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad .. (2)$$

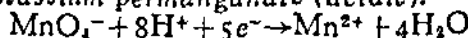
(*d*) Adding up (1) and (2) :


$$H_2C_2O_4 + H_2O_2 \rightarrow 2CO_2 + 2H_2O$$

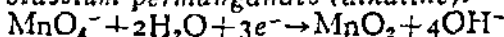
Half-reactions of some important oxidizing and reducing agents sed in volumetric analysis are given below for ready reference :

Oxidizing agents :

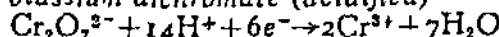
(*i*) *Potassium permanganate (acidic).*


$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

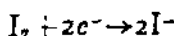
(*ii*) *Potassium permanganate (alkaline).*


$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

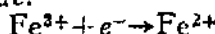
(*iii*) *Potassium dichromate (acidified)*


$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

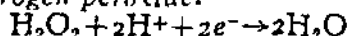
(*iv*) *Iodine.*


$$I_2 + 2e^- \rightarrow 2I^-$$

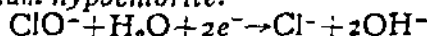
(*v*) *Ferric chloride.*


$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

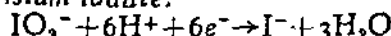
(*vi*) *Hydrogen peroxide.*


$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

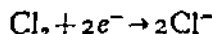
(*vii*) *Sodium hypochlorite.*


$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$$

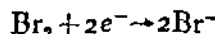
(*viii*) *Potassium iodate.*


$$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$$

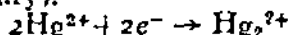
(*ix*) *Chlorine.*

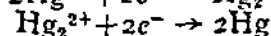

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

(*x*) *Bromine.*

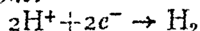

$$Br_2 + 2e^- \rightarrow 2Br^-$$

(*xi*) *Mercuric salts* (two stages of reduction—to mercurous alts and to mermury).


$$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$$

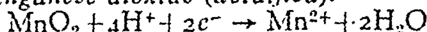

$$Hg_2^{2+} + 2e^- \rightarrow 2Hg$$

(*xii*) *Hydrogen ions.*



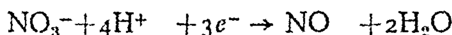
$$2H^+ + 2e^- \rightarrow H_2$$

(*xiii*) *Manganese dioxide (acidified).*

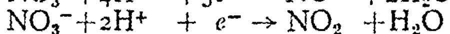


$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

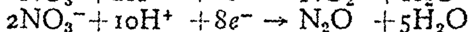
(*xiv*) *Nitric acid.* It can be reduced to various stages given below :



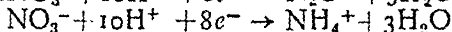
$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$



$$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$$



$$2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$$



$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$$

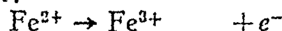
Reducing agents :

(*i*) *Oxalic acid.*



$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

(*ii*) *Ferrous sulphate.*



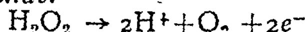
$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

(*iii*) *Sodium thiosulphate.*



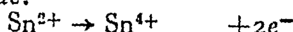
$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$$

(*iv*) *Hydrogen peroxide.*



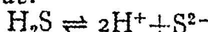
$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$$

(*v*) *Stannous chloride.*



$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

(*vi*) *Hydrogen sulphide.*



$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$



$$S^{2-} \rightarrow S + 2e^-$$

(*vii*) *Sulphurous acid.*



$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$$

(*viii*) *Hydriodic acid.* (Acidified potassium iodide solution).



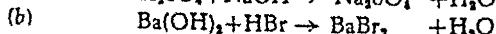
$$2I^- \rightarrow I_2 + 2e^-$$

QUESTIONS

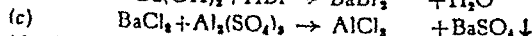
1. Balance the following equations by hit and trial method and rewrite them in the ionic form :



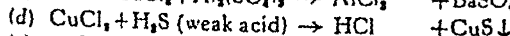
(*a*) $H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$



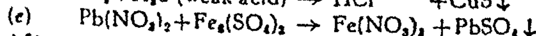
(*b*) $Ba(OH)_2 + HBr \rightarrow BaBr_2 + H_2O$



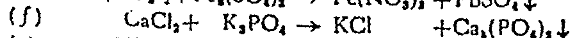
(*c*) $BaCl_2 + Al_2(SO_4)_3 \rightarrow AlCl_3 + BaSO_4\downarrow$



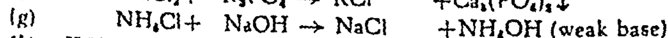
(*d*) $CuCl_2 + H_2S$ (weak acid) $\rightarrow HCl + CuS\downarrow$



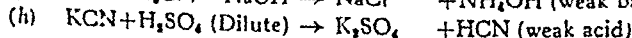
(*e*) $Pb(NO_3)_2 + Fe_2(SO_4)_3 \rightarrow Fe(NO_3)_3 + PbSO_4\downarrow$



(*f*) $CaCl_2 + K_3PO_4 \rightarrow KCl + Ca_3(PO_4)_2\downarrow$

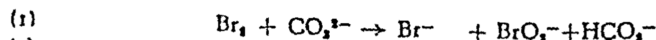


(*g*) $NH_4Cl + NaOH \rightarrow NaCl + NH_4OH$ (weak base)

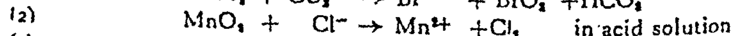


(*h*) $KCN + H_2SO_4$ (Dilute) $\rightarrow K_2SO_4 + HCN$ (weak acid)

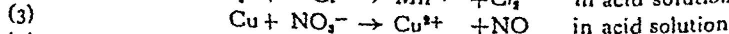
2. Complete and/or balance the following equations by the ion-electron method :



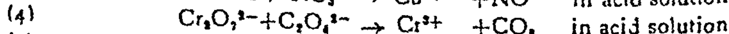
(1) $Br_2 + CO_3^{2-} \rightarrow Br^- + BrO_3^- + HCO_3^-$



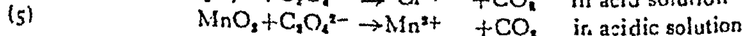
(2) $MnO_4^- + Cl^- \rightarrow Mn^{2+} + Cl_2$ in acid solution



(3) $Cu + NO_3^- \rightarrow Cu^{2+} + NO$ in acid solution



(4) $Cr_2O_7^{2-} + C_2O_4^{2-} \rightarrow Cr^{3+} + CO_2$ in acid solution



(5) $MnO_2 + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$ in acidic solution

(6) $MnO_4^- + SO_3^{2-} \rightarrow MnO_4^{2-} + SO_4^{2-}$

(7) $S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + I^-$ in basic solution

(8) $Cr_2O_7^{2-} + Fe^{2+} + C_2O_4^{2-} \rightarrow Cr^{3+} + Fe^{3+} + CO_2$ in acidic solution

(9) $P_4 \rightarrow H_2PO_2^- + PH_3$ in basic solution

(10) $MnO_4^{2-} \rightarrow MnO_4^- + MnO_2$ in acid solution

(11) $I_2 + NO_3^- \rightarrow NO_2 + IO_3^-$ in acid solution

3. Balance the following equations by the ion-electron method :

(1) $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$

(2) $H_3AsO_4 + KI + HCl \rightarrow H_3AsO_3 + KCl + I_2 + H_2O$

(3) $K_2Cr_2O_7 + KI + HCl \rightarrow I_2 + CrCl_3 + H_2O$

(4) $SbCl_5 + KI \rightarrow SbCl_3 + I_2 + KCl$

(5) $FeCl_3 + SnCl_2 \rightarrow SnCl_4 + FeCl_2$

(6) $CaC_2O_4 + H_2SO_4 + KMnO_4 \rightarrow CaSO_4 + K_2SO_4 + MnSO_4 + CO_2 + H_2O$

(7) $H_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + HI$

(8) $KNO_2 + KMnO_4 + H_2SO_4 \rightarrow KNO_3 + K_2SO_4 + MnSO_4 + H_2O$

(9) $KMnO_4 + SbCl_3 + HCl \rightarrow KCl + MnCl_2 + SbCl_5 + H_2O$

(10) $NaClO_3 + KI + HCl \rightarrow NaCl + I_2 + KCl + H_2O$

(11) $Ce(SO_4)_2 + H_2C_2O_4 \rightarrow Ce_2(SO_4)_3 + H_2SO_4 + CO_2$

(12) $As + HNO_3 + H_2O \rightarrow H_3AsO_4 + NO$

(13) $Ag + HNO_3 + HNO_3 \rightarrow AgNO_3 + NO + H_2O$

(14) $CuS + HNO_3 + HNO_3 \rightarrow Cu(NO_3)_2 + S + NO + H_2O$

(15) $H_2C_2O_4 + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + CO_2 + K_2SO_4$

(16) $Sn + HNO_3 \rightarrow SnO_2 + NO + H_2O$

(17) $PbCrO_4 + H_2SO_4 + FeSO_4 \rightarrow Fe_2(SO_4)_3 + PbSO_4 + Cr_2(SO_4)_3 + H_2O$

(18) $SbCl_3 + KIO_3 + HCl \rightarrow SbCl_5 + KI + H_2O$

(19) $Fe_2(SO_4)_3 + H_2SO_3 + H_2O \rightarrow FeSO_4 + H_2SO_4 + H_2SO_4$

(20) $SnCl_2 + HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2$

4. Balance the following equations by the ion-electron method ·

(1) $Cr_2(SO_4)_3 + KMnO_4 + H_2O \rightarrow H_2Cr_2O_7 + H_2SO_4 + MnSO_4 + K_2SO_4$

(2) $SbCl_3 + KBrO_3 + HCl \rightarrow SbCl_5 + KBr + H_2O$

(3) $SnCl_2 + I_2 + HCl \rightarrow SnCl_4 + HI$

(4) $FeCl_2 + K_2Cr_2O_7 + HCl \rightarrow FeCl_3 + CrCl_3 + KCl + H_2O$

(5) $KI + KIO_3 + HCl \rightarrow I_2 + KCl + H_2O$

(6) $H_2CrO_4 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + H_2O$

(7) $KNO_2 + KI + HCl \rightarrow KCl + I_2 + NO + H_2O$

(8) $Ce(SO_4)_2 + FeSO_4 \rightarrow Fe_2(SO_4)_3 + Ce_2(SO_4)_3$

(9) $HNO_3 + H_2S \rightarrow NO + H_2SO_4 + H_2O$

(10) $Cu + HNO_3 + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

(11) $H_2SO_4 + HI \rightarrow H_2S + H_2O + I_2$

(12) $KI + KIO_3 + H_2SO_4 \rightarrow I_2 + K_2SO_4 + H_2O$

(13) $MnO_2 + FeSO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O$

(14) $Ce(SO_4)_2 + H_3AsO_3 + H_2O \rightarrow H_3AsO_4 + Ce_2(SO_4)_3 + H_2SO_4$

(15) $H_2S + H_2SO_4 + KMnO_4 \rightarrow K_2SO_4 + MnSO_4 + S + H_2O$

(16) $Cu + HNO_3 + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

(17) $Zn + HNO_3 + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$

(14) $S^{2-} \rightarrow S + 2e^-] \times 3$

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \times 2$

$3S^{2-} + 2NO_3^- + 8H^+ \rightarrow 3S + 2NO + 4H_2O$

(15) $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$

$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

(16) $Sn + 2H_2O \rightarrow SnO_2 + 4H^+ + 4e^-] \times 3$

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O] \times 4$

$3Sn + 4NO_3^- + 4H^+ \rightarrow 3SnO_2 + 4NO + 2H_2O$

(17) $CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 3$

$CrO_4^{2-} + 3Fe^{2+} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O$

(18) $SbCl_3 + 2Cl^- \rightarrow SbCl_5 + 2e^-] \times 3$

$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$

$3SbCl_3 + 6Cl^- + IO_3^- + 6H^+ \rightarrow 3SbCl_5 + I^- + 3H_2O$

(19) $Fe^{3+} + e^- \rightarrow Fe^{2+}] \times 2$

$H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

$2Fe^{3+} + H_2SO_3 + H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} 4H^+$

(20) $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$

$Sn^{2+} + 2Hg^{2+} \rightarrow Sn^{4+} + Hg_2^{2+}$

4. (1) $2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-] \times 5$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 6$

$10Cr^{3+} + 6MnO_4^- + 11H_2O \rightarrow 5Cr_2O_7^{2-} + 6Mn^{2+} + 22H^+$

(2) $SbCl_3 + 2Cl^- \rightarrow SbCl_5 + 2e^-] \times 3$

$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$

$3SbCl_3 + 6Cl^- + BrO_3^- + 6H^+ \rightarrow 3SbCl_5 + Br^- + 3H_2O$

(3) $SnCl_2 + 2Cl^- \rightarrow SnCl_4 + 2e^-$

$I_2 + 2e^- \rightarrow 2I^-$

$SnCl_2 + I_2 + 2Cl^- \rightarrow SnCl_4 + 2I^-$

(4) $Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 6$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(5) $2I^- \rightarrow I_2 + 2e^-] \times 5$

$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

$10I^- + 2IO_3^- + 12H^+ \rightarrow 6I_2 + 6H_2O$

or $5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

(6) $2CrO_4^{2-} 16H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-] \times 6$

$2CrO_4^{2-} + 16H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 8H_2O + 6Fe^{3+}$

(7) $NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O] \times 2$

$2I^- \rightarrow I_2 + 2e^-$

$2NO_2^- + 4H^+ + 2I^- \rightarrow 2NO + 2H_2O + I_2$

(8) $Ce^{4+} + e^- \rightarrow Ce^{3+}$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

(9) $H_2S + 4H_2O \rightarrow SO_4^{2-} + 10H^+ + 8e^-] \times 3$

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad] \times 8$

$3H_2S + 8NO_3^- + 2H^+ \rightarrow 3SO_4^{2-} + 8NO + 4H_2O$

(10) $Cu \rightarrow Cu^{2+} + 2e^- \quad] \times 3$

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad] \times 2$

$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$

(11) $2I^- \rightarrow I_2 + 2e^- \quad] \times 4$

$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$

$8I^- + SO_4^{2-} + 10H^+ \rightarrow 4I_2 + H_2S + 4H_2O$

(12) Same as (5) above.

(13) $MnO_2+4H^++2e^-\rightarrow Mn^{2+}+2H_2O$
$Fe^{2+}\rightarrow Fe^{3+}+e^-]\times 2$
$MnO_2+2Fe^{2+}+4H^+\rightarrow Mn^{2+}+2Fe^{3+}+2H_2O$

(14) $H_3AsO_3+H_2O\rightarrow H_3AsO_4+2H^++2e^-$
$Ce^{4+}+e^-\rightarrow Ce^{3+}\quad]\times 2$
$H_3AsO_3+H_2O+2Ce^{4+}\rightarrow H_3AsO_4+2H^++2Ce^{3+}$

(15) $H_2S\rightarrow S+2H^++2e^-\quad]\times 5$
$MnO_4^-+8H^++5e^-\rightarrow Mn^{2+}+4H_2O\quad]\times 2$
$5H_2S+2MnO_4^-+6H^+\rightarrow 5S+2Mn^{2+}+8H_2O$

(16) $Cu\rightarrow Cu^{2+}+2e^-$
$NO_3^-+2H^++e^-\rightarrow NO_2+H_2O\quad]\times 2$
$Cu+2NO_3^-+4H^+\rightarrow Cu^{2+}+2NO_2+2H_2O$

(17) $Zn\rightarrow Zn^{2+}+2e^-$
$NO_3^-+10H^++8e^-\rightarrow NH_4^++3H_2O$
$4Zn+NO_3^-+10H^+\rightarrow 4Zn^{2+}+NH_4^++3H_2O$

(18) $H_2O_2+2H^++2e^-\rightarrow 2H_2O$
$2I^-\rightarrow I_2+2e^-$
$H_2O_2+2H^++2I^-\rightarrow 2H_2O+I_2$

(19) $H_2O_2\rightarrow O_2+2H^++2e^-$
$Ce^{4+}+e^-\rightarrow Ce^{3+}\quad]\times 2$
$H_2O_2+2Ce^{4+}\rightarrow O_2+2H^++2Ce^{3+}$

(20) $H_2SO_3+H_2O\rightarrow SO_4^{2-}+4H^++2e^-]\times 3$
$NO_3^-+4H^++3e^-\rightarrow NO+2H_2O\quad]\times 2$
$3H_2SO_3+2NO_3^-\rightarrow 3SO_4^{2-}+4H^++2NO+H_2O$

(21) $H_3AsO_3+H_2O\rightarrow H_3AsO_4+2H^++2e^-]\times 5$
$MnO_4^-+8H^++5e^-\rightarrow Mn^{2+}+4H_2O\quad]\times 2$
$5H_3AsO_3+2MnO_4^-+6H^+\rightarrow 5H_3AsO_4+2Mn^{2+}+3H_2O$

5. (i) $I_2+2e^-\rightarrow 2I^-$
$2S_2O_3^{2-}\rightarrow S_4O_6^{2-}+2e^-$
$2S_2O_3^{2-}+I_2\rightarrow S_4O_6^{2-}+2I^-$
Oxidised *Reduced*

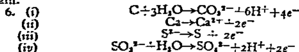
(ii) $2Na\rightarrow 2Na^++2e^-$
$Cl_2+2e^-\rightarrow 2Cl^-$
$2Na+Cl_2\rightarrow 2Na^++2Cl^-$
Oxidised *Reduced*

(iii) $Sn^{2+}\rightarrow Sn^{4+}+2e^-$
$Hg^{2+}+2e^-\rightarrow Hg$
$Sn^{2+}+Hg^{2+}\rightarrow Sn^{4+}+Hg$
Oxidised *Reduced*

(iv) $Zn\rightarrow Zn^{2+}+2e^-$
$2H^++2e^-\rightarrow H_2$
$Zn+2H^+\rightarrow Zn^{2+}+H_2$
Oxidised *Reduced*

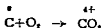
(v) $2Fe^{2+}\rightarrow 2Fe^{3+}+2e^-$
$Br_2+2e^-\rightarrow 2Br^-$
$2Fe^{2+}+Br_2\rightarrow 2Fe^{3+}+2Br^-$
Oxidised *Reduced*

Reason in each case being definitions of oxidation and reduction. *Oxidation is the process of electron-loss* while Reduction is the process of electron-gain.


6. (i) $C+3H_2O\rightarrow CO_3^{2-}+6H^++4e^-$
(ii) $Ca\rightarrow Ca^{2+}+2e^-$
(iii) $S^{2-}\rightarrow S+2e^-$
(iv) $SO_3^{2-}+H_2O\rightarrow SO_4^{2-}+2H^++2e^-$

or Oxidation number of carbon changes from 0 (in C) to—4 (in CO_2). Hence it is a case of oxidation.

Oxidation Number


$$\overset{0}{C}+O_2\rightarrow \overset{4+}{CO_2}$$

Appendix III

WHAT HAPPENS

1. Explain, giving equations, what happens when—

(*a*) Burning magnesium is introduced into a jar of carbon dioxide.

(*b*) Hydrogen sulphide is passed through an acidified solution of copper sulphate.

(*c*) A mixture of sodium chloride and manganese dioxide is heated with concentrated sulphuric acid.

(*d*) Chloride is passed through a solution of sodium hydroxide.

(*e*) Phosphorus is heated with caustic potash.

(*All India H.S. 1967*)

2. Describe, giving equations, what happens when—

(*a*) Hydrogen sulphide is passed through an aqueous solution sulphur dioxide.

(*b*) Chlorine is passed through an aqueous solution of sodium hydroxide.

(*c*) Nitric oxide is passed through a solution of ferrous sulphate.

(*d*) Phosphorus is treated with caustic potash.

(*e*) Carbon dioxide is passed through a solution of calcium hydroxide. (*All India H.S. 1966*)

3. Describe, giving equations, what happens when—

(*a*) Burning magnesium wire is introduced into a jar of carbon dioxide.

(*b*) Hydrogen sulphide is passed through an acidified solution of copper sulphate.

(*c*) A mixture of sodium chloride and manganese dioxide is heated with concentrated sulphuric acid.

(*d*) Chlorine is passed through a hot and concentrated solution of caustic soda.

(*e*) Phosphorus is heated with caustic potash solution.

(*Delhi H.S. 1971*)

4. Explain, giving equations, what happens when—

(*a*) Ammonium hydroxide is added to a mixture of silver chloride and mercurous chloride.

(*b*) Sodium nitrate solution is heated with ammonium chloride.

(*c*) Stannous chloride solution is treated with excess of sodium hydroxide solution.

(*d*) Potassium permanganate is treated with hydrochloric acid.

(*e*) Ozone is treated with ethylene. (*Delhi Pre-Medical 1963*)

5. Explain, giving equations, what happens when—

(*a*) Sodium peroxide reacts with acidified potassium permanganate.

(*b*) Calcium phosphate reacts with sulphuric acid.

(*c*) Hydrogen sulphide is passed through an acidified solution of copper sulphate.

(*d*) Ozone is made to pass through a solution of potassium iodide. (*Delhi H.S. 1963*)

6. State, giving equations, what happens when—

[illegible] heated (*i*) alone ; (*ii*) with potas- [illegible] ...entrated sulphuric acid ; (*iv*) with [illegible]

(*b*) Aluminium is treated with dilute sulphuric acid.

(*c*) Hydrogen peroxide is added to a solution of potassium permanganate acidified with dilute sulphuric acid.
(*Punjab Pre-University 1963*)

7. What happens when the following substances are heated—

(*i*) Potassium nitrate ;	(*ii*) Copper nitrate ;
(*iii*) Lead nitrate ;	(*iv*) Sodium nitrate ;
(*v*) Silver nitrate ;	(*vi*) Barium nitrate ;
(*vii*) Mercuric nitrate ;	(*viii*) Ammonium nitrate ;
(*ix*) Ammonium chloride ;	(*x*) Ammonium dichromate ;
(*xi*) Ammonium nitrite ;	(*xii*) Potassium chlorate ;
(*xiii*) Barium carbonate ;	(*xiv*) Zinc carbonate ;
(*xv*) Sodium bicarbonate :	(*xvi*) Sodium formate ;
(*xvii*) Phosphoric acid ;	(*xviii*) Crystalline copper sulphate.

(*Delhi H.S. 1963*)

8. What happens when—

(*a*) Carbon dioxide solution is bubbled through sodium hydroxide solution.

(*b*) Sodium sulphite solution is boiled with sulphur.

(*c*) Sodium peroxide is treated with dilute sulphuric acid.

(*d*) Copper is heated with concentrated nitric acid.

(*e*) Sodium nitrate is treated with dilute sulphuric acid.

(*f*) Zinc is heated with concentrated sulphuric acid.

(*g*) Aluminium hydroxide is heated with caustic soda solution. (*All India H.S. 1971*)

9. State with equations what happens when—

(*a*) Copper is heated with nitric acid.

(*b*) Iodine is added to a solution of sodium thiosulphate.

(*c*) Ammonium nitrite is heated.

(*d*) Sulphur dioxide is passed through a solution of potassium dichromate and dilute sulphuric acid. (*Delhi Pre-University 1960*)

10. State with equations what happens when—

(*a*) Carbon dioxide is passed through lime water.

(*b*) Oxalic acid is heated with concentrated sulphuric acid.

(*c*) Hydrogen sulphide is passed into sulphurous acid.

(*d*) Ammonium nitrate is heated.

(*Delhi Pre-University 1961*)

11. Explain, giving equations, what happens when—

(*i*) White phosphorus is heated with strong solution of sodium hydroxide.

(*ii*) Chlorine is passed through hot not concentrated solution of sodium hydroxide.

(*iii*) Hydrogen peroxide is added to potassium permanganate solution containing dilute sulphuric acid.

(*iv*) Excess of ammonia solution is added to a solution of silver nitrate. (*Delhi Pre-Medical 1960*)

12. Explain, giving equations, what happens when—

(*a*) Copper is made to react with concentrated sulphuric acid.

(*b*) Aluminium is acted upon by caustic soda solution.

(*c*) Zinc sulphate is made to react with sodium bicarbonate.

(*d*) Sodium thiosulphate is reacted with solution of iodine.

(*e*) Lead peroxide is heated with hot concentrated hydrochloric acid. (*Delhi H.S. 1964*)

13. What happens when :

(*a*) Zinc metal is heated with dilute nitric acid.

(*b*) Sodium bicarbonate is strongly heated.

(*c*) An iron rod is kept in copper sulphate solution.

(*d*) Potassium iodide is heated with sulphuric acid.

(*e*) Sodium hydroxide is added to ferrous sulphate solution.

(*f*) Calcium carbide is treated with water.

(*All India H.S. 1970*)

Appendix IV

TYPICAL CONVERSIONS

1. How may any three of the following conversions be carried out ?

(i) Potassium hydroxide to potassium chlorate.

(ii) Iron to ferric chloride.

(iii) Mercury to mercuric chloride.

(iv) Sodium hydroxide to sodium thiosulphate.

(*Delhi H.S.* 1971)

2. How may any four of the following conversions be carried out ?

(i) Aluminium to anhydrous aluminimum chloride.

(ii) Mercury to calomel.

(iii) Copper to copper sulphate.

(iv) Cast iron to wrought iron.

(v) Sodium chloride to sodium bicarbonate.

(*Delhi H S.* 1970)

3. Describe giving chemical equations how we can obtain :

(i) Ferric chloride from iron.

(ii) Calomel from mercury.

(iii) Potassium chlorate from sodium chloride.

(iv) Copper sulphate from copper scrap.

(v) White lead from lead. (*Delhi H.S.* 1969)

4. Describe the following—

(a) Preparation of potassium chlorate starting with sodium hydroxide.

(b) Conversion of silver nitrate into silver.

(c) Preparation of anhydrous ferric chloride from iron powder.

(d) Preparation of white lead from lead.

(*All India H.S.* 1971)

5. Describe how the following are obtained—

(a) Metallic silver from silver nitrate.

(b) Zinc from zinc oxide.

(c) Copper from copper sulphate.

(d) Mercurous chloride from mercuric chloride.

(*All India H.S.* 1969)

6. Explain briefly how can you obtain any four of the following substances.

(*a*) Mercury from mercuric chloride.

(*b*) Zinc oxide from zinc sulphide.

(*c*) Silver from silver residues.

(*d*) Sodium hydroxide from sodium carbonate.

(*e*) Potassium chloride from potassium iodide.

7. How can you prepare the following :

(*i*) $NaHCO_3$ from Na_2CO_3 ;

(*ii*) $CuSO_4$ from Cu ;

(*iii*) $Ba(NO_3)_2$ from $BaCl_2$;

(*iv*) NH_4Cl from $(NH_4)_2SO_4$;

(*v*) $FeSO_4$ from $Fe_2(SO_4)_3$?

8. How would you prepare the following :

(*a*) Strontium nitrate from strontium sulphate ;

(*b*) Zinc oxide from zinc chloride ;

(*c*) Nitrogen from nitric oxide ;

(*d*) Aluminium sulphate from alum ;

(*e*) Carbon from carbon monoxide ?

9. How would you obtain :

(*i*) Mercuric oxide from mercuric chloride ;

(*ii*) Oxygen from nitric acid ;

(*iii*) Antimony sulphide from its oxide :

(*iv*) Silver bromide from silver ?

10. Starting from zinc carbonate, how will you obtain (*i*) zinc nitrate, (*ii*) zinc oxide, (*iii*) zinc sulphate, and (*iv*) anhydrous zinc chloride ?

11. How would you demonstrate the truth of the following statements :

(*a*) Caustic soda contains hydrogen.

(*b*) Hypo contains sulphur.

(*c*) Nitre contains oxygen.

(*d*) Bleaching powder contains chlorine ? Give equations for the reactions.

12. How would you obtain from tin (*a*) Stannic oxide, (*b*) Stannic chloride ?

13. How would you obtain the following :

(*a*) Nitrogen from ammonia and *vice versa*.

(*b*) Chlorine from hydrochloric acid and *vice versa*.

(c) Carbon from carbon dioxide and *vice versa.*

(d) Sulphur from hydrogen sulphide and *vice versa.*

Give only the conditions and chemical equations for the above changes.

14. How would you prepare the following :

(a) Cuprous oxide from copper sulphate.

(b) Barium nitrate from barium chloride.

(c) Ferric sulphate from ferric chloride.

(d) Lead sulphate from lead.

(e) Calomel from corrosive sublimate.

15. How will you obtain :

(a) Steel from cast iron.

(b) Oxygen from nitric acid.

(c) Zinc sulphide from zinc chloride solution.

(d) Barium oxide from barium chloride solution.

(e) Cuprous chloride from copper oxide.

16. How will you obtain :

(a) Copper sulphate from a solution of copper nitrate.

(b) Bromine from potassium bromide.

(c) Magnesium chloride from magnesium carbonate.

(d) Anhydrous aluminium chloride from aluminium.

17. Starting with zinc, how would you prepare :

(a) Zinc oxide ; (b) Anhydrous zinc chloride ; (c) Zinc sulphate ?

18. State briefly how any three of the following are obtained :

(a) Nitric acid from ammonia.

(b) Calcium carbide from limestone.

(c) Potassium dichromate from chromite ore.

(d) Hydrogen iodide from iodine ? (*Delhi Pre-Medical 1960*)

19. How would you prepare the following :

(a) Cuprous chloride from copper sulphate.

(b) Bleaching powder from lime.

(c) Strontium chloride from strontium nitrate.

(d) Magnesium phosphate from magnesium carbonate.

(e) Silver oxide from silver nitrate ? (*U.P. Board Inter. 1960*)

DO YOU KNOW

1. Do you know why—

(*a*) Water which contains 80% oxygen is used as a fire extinguisher.

(*b*) A solution of copper sulphate behaves acidic towards litmus.

(*c*) Dry chlorine cannot bleach clothes.

(*d*) Phosphorus glows in dark.

(*e*) Hydrogen sulphide cannot be dried by passing through conc. sulphuric acid.

(*f*) Lime water first becomes milky and then clear when carbon dioxide is passed through it.

(*g*) Hard water softens on boiling.

(*h*) Hydrogen and sulpur dioxide are reducing agents.
(*Punjab H.S. 1963*)

2. Give reasons with equations, if any, for the following :

(*a*) Sugar gets charred when it is treated with concentrated sulphuric acid.

(*b*) Caustic soda has to be melted before it can be used for the extraction of sodium metal electrolytically.

(*c*) An iodide solution turns brown on treatment with acidified potassium permanganate solution.

(*d*) Dilute nitric acid cannot be used for the preparation of hydrogen sulphide gas.

(*e*) Sometimes a black residue is left in the flask in which sulphur dioxide gas is prepared by heating copper turnings with concentrated sulphuric acid. (*Punjab Pre-University 1963*)

3. Give reasons with equations, if any, for the following :

(*a*) Chlorine cannot be used for bleaching a dry piece of cloth.

(*b*) A fresh iodine stain can be removed by washing with hypo.

(*c*) An inert atmosphere is required for the preparation of phosphine in the laboratory.

(*d*) Iodine and not hydriodic acid is produced by heating an iodide with concentrated sulphuric acid.

(*e*) In contact process for the manufacture of sulphuric acid, sulphur trioxide is not directly dissolved in water.

(*f*) Fused calcium chloride cannot be used for drying ammonia gas. (*Punjab Pre-University 1962*)

4. Explain any three of the following :

(*a*) Why is a reddish-brown solution of bromine water decolorised by the addition of caustic soda solution ?

(b) Why is it more dangerous to ignite a mixture of hydrogen and oxygen than to ignite pure hydrogen ?

(c) Why does concentrated nitric acid often turn yellow on standing ?

(d) Why is phosphorus not found free in nature ?
(*Delhi H.S. 1964*)

5. Correct the following statements giving appropriate nswers in not more than two lines :

(a) Concentrated sulphuric acid reacts with zinc to give ydrogen sulphide.

(b) Ozone is a reducing agent.

(c) Hydrogen peroxide decomposes on heating to give hy-rogen and oxygen.

(d) Water gas is a mixture of carbon monoxide and nitrogen.

(e) Organic compounds are electrovalent in nature.

(f) The allotropes of carbon are physically identical.
(*All India H.S. 1966*)

6. Do you agree with the following statements ? Give asons briefly :

(i) All atoms of an element are alike in all the physical and emical properties.

(ii) The conversion of ferrous ion to ferric ion involves a ange at the iron nucleus.

(iii) The atomic weight, molecular weight and equivalent eight of sulphur have fixed values.

(iv) At N.T.P. 100 c.c. of hydrogen gas contains twice as any atoms of hydrogen as are contained in 100 c.c. of hydrogen loride gas.

(v) Zinc will not dissolve in mercury.

(vi) Aluminium is replacing copper in electrical goods be-use of its better electrical conductance. (*All India H.S. 1967*)

7. Correct the following statements giving appropriate swers in not more than two lines :-

(a) Petroleum is obtained by crushing oil seeds.

(b) Ethane is an element.

(c) Water is a mechanical mixture containing hydrogen and ygen.

(d) The allotropes of sulphur are physically identical.

(e) Bleaching powder is made by the action of hydrogen loride on slaked lime.

(f) Glass is a chemical compound of silicates of calcium and dium ? (*All India H.S. 1967*)

8. Which of the following statements are correct and whi are not correct? Give reasons very briefly in support of yo answer in each case :

(*a*) Ammonia can be dried by passing over phosphorus pent oxide.

(*b*) A solution of ferric chloride has no action on litmus.

(*c*) Carbon dioxide is of no use to living organisms.

(*d*) A solution of sulphur dioxide has no action on litm solution.

(*e*) Carbon dioxide does not allow anything to burn in it.

(*f*) Phosphorus occurs free in nature.

(*g*) Chlorine is found near open drains.

(*h*) All solutions contain ions. (*Delhi H.S. 196*

9. Correct the following statements giving appropria reasons in not more than two lines :

(*a*) Conversion of water into steam is a chemical change.

(*b*) A molecule of hydrogen contains one atom.

(*c*) Covalent compounds are ionised in solution.

(*d*) Potassium chlorate is a strong reducing agent.

(*e*) Equivalent weight of a compound is twice its vapo density.

(*f*) Atomic weight is the basis of modern Periodic classific tions. (*Delhi H.S. 197*

10. Give brief explanations for the following :

(*i*) Aluminium vessels are not used for heating alkali substances.

(*ii*) Lead chambers are used in the manufacture of sulphur acid.

(*iii*) Potassium carbonate is not made by the Solvay so process.

(*iv*) A solution of sodium thio-sulphate dissolves silv chloride.

(*v*) Sodium is prepared by the electrolysis of molten sodiu chloride and not of its solution in water.

(*vi*) The exposed film taken out from a camera does not ha any visible impression on it. (*Delhi H.S. 196*

11. Correct the following statements wherever necessar giving reasons :

(*a*) Organic compounds are electrovalent.

(*b*) Hydrogen peroxide has no action on acidified potassiu permanganate solution.

(*c*) Nitric oxide is obtained when copper is heated wi concentrated sulphuric acid.

Appendix VI

QUALITATIVE ANALYSIS

1. How would you test for and distinguish between :

(*a*) Fluoride and chloride ;

(*b*) Nitrate and nitrite ;

(*c*) The ortho-, meta- and pyrophosphates of sodium ;

(*d*) Sulphates and sulphites ?

2. Give all the tests you would perform to distinguish between :

(*a*) A bromide and an iodide ;

(*b*) A ferrous salt and a ferric salt ;

(*c*) A mercurous salt and a mercuric salt ;

(*d*) Stannous and stannic salts.

3. How will you distinguish :

(*a*) Carbonate from a bicarbonate ;

(*b*) Sulphide from a sulphite ;

(*c*) A chloride and a chlorate ;

(*d*) Sulphate and thiosulphate ;

(*e*) Chloride, bromide and iodide ;

(*f*) Sulphite, thiosulphate and sulphate ?

4. Write a short note on the principles on which tables of analysis are based.

5. Explain fully the reactions which are utilised to distinguish between the following pairs of ions when present together in a solution :

(*a*) Copper and cadmium ;

(*b*) Zinc and aluminium ;

(*c*) Potassium carbonate in caustic potash ;

(*d*) Chlorine in hydrochloric acid.

6. By what chemical tests would you distinguish between :

(*a*) A nitrite, a nitrate and a bromide ;

(*b*) Sulphite and sulphate ;

(*c*) Ferrous and ferric salts ;

(*d*) An arsenite, an arsenate and a phosphate ;

(*e*) A bicarbonate, a carbonate and an oxalate ?

7. Indicate clearly what qualitative experiments would you perform to distinguish between :

(*a*) Two sulphates of iron ;

(*b*) Two nitrates of mercury ;

(c) Two chlorides of tin ;

(d) Potassium chlorate and potassium chloride ;

(e) Four unlabelled bottles each containing one of the following salts : (i) K_2CO_3 ; (ii) $NaHCO_3$; (iii) $Na_2S_2O_3$; and (iv) K_2S.

(f) Three jars containing hydrogen, carbon monoxide and ntirous oxide.

8. How will you distinguish between *sodium chloride*, potassium chloride and ammonium chloride ?

9. How would you account for the following :

(i) A solution is boiled with nitric acid before proceeding with group III of analysis.

(ii) Use of NH_4Cl in group III and use of NH_4Cl+NH_4OH in group IV of analysis.

(iii) Before passing H_2S, the solution must be acidic in group II and ammoniacal in group IV.

(iv) Sometimes a white precipitate appears in group I even when Pb, Ag, and Hg_2^{2+} are absent.

(v) Sometimes a yellowish precipitate appears in group II and it cannot be due to Cd, As or Sn (ic).

(vi) A white crystalline precipitate appears on adding HCl to a barium chloride solution.

(vii) A paste of salt is prepared in concentrated hydrochloric acid for flame test.

10. Explain the use of the following in qualitative chemical analysis :

(i) Hydrogen sulphide ; (ii) Borax ;

(iii) Ammonium chloride.

11. Explain with the help of equations a sensitive test that be employed for detecting :

(a) Traces of ammonium chloride in brine.

(b) Slightly oxidised ferrous sulphate.

(c) 1% KBr as impurity in potassium chloride.

(d) Sodium sulphite in admixture with sodium sulphate.
(*Punjab Inter.* 1960)

Appendix VII

GLOSSARY

Abrasive. A hard substance with sharp edges, used for polishing and grinding.

Absolute Temperature. Temperature measured on the absolute scale and is the Centigrade temperature plus 273. $A = C + 273$.

Absolute Zero. Lowest possible temperature at which all molecular motion will probably cease. It is equal to $-273°C$.

Acid. A chemical compound which in water solution forms no positive ions except H^+ ions.

Acid Anhydride. The oxide of a non-metal which combines with water to form an acid.

Acid Salt. A salt which is formed by an incomplete neutralization of an acid still contains replaceable hydrogen.

Alcohol. An organic compound containing hydroxyl group and derived from a hydrocarbon.

Alkali. The water soluble base.

Allotropy. Phenomenon of existence of an element in more than one form.

Alloy. A solid solution of one or more metals in another metal.

Alpha Particle. A helium atom carrying two units of positive charge, emitted during radioactive distintegrations.

Alum. A double sulphate of monovalent metal (X) and a trivalent metal (Y) with general formula, $X_2SO_4.Y_2(SO_4)_3.24H_2O$.

Amalgam. An alloy of mercury with one or more metals.

Amorphous. Without definite shape.

Ampere. Strength of the current which deposits 0·001118 gm. of silver per second or sends one coulomb of electricity per second.

Amphoteric. Substance which acts both as an acid as well as a base.

Analysis. Breaking a part of chemical compound in order to determine its composition.

Anaesthetic. Anything that causes unconsciousness.

Anhydrous. Free from water.

Anion. Negatively-charged ion which moves towards the *anode* (positive electrode) during electrolysis.

Annealing. A regulated heat treatment used for toughening materials, *e.g.*, glass.

Antichlor. A substance used for removing excess of chlorine during bleaching, *e.g.*, sodium sulphide or hypo.

Antidote. A substance used to counteract the effect of a posion.

Antiseptic. Substances which prevent the growth of harmful micro-organisms in living tissues.

Aqua Regia. A mixture of concentrated nitric and hydrochloric acid in the ratio 1 : 3.

Atmosphere. The envelope of air completely surrounding the earth to a depth of many miles and exerting an everage pressure of 14·7 pounds per square inch or 760 mm. column of mercury.

Atom. The smallest particle of an element which may or may not be capable of independent existence.

Atomic Number. The net positive charge on the nucleus of an atom.

Atomic Weight. The average, relative weight of an atom compared with that of carbon atom taken as 12.

Avogadro's Number. The number of molecules present in one gram molecular weight of any gas, liquid or solid ($=6{\cdot}023\times10^{23}$).

Baking Powder. A leavening mixture (*e.g.*, Starch + Sodium bicarbonate + Potassium acid tartrate).

Baking Soda. Sodium bicarbonate.

Base. A substance which in aqueous solution forms no negative ions other than OH^- ions.

Basic Anhydride. The oxide of a metal which unites with water to form a base.

Basic Salt. A salt which is produced by an incomplete neutralization of a base and still contains some replaceable hydroxyl groups.

Beta rays. A stream of electrons emitted during radioactive disintegrations.

Bleaching. Changing naturally coloured substance to colourless.

Binary Compounds. Compounds made up of only two elements.

Boiler scale. A deposit of calcium or magnesium salts formed in boilers using hard water.

Carat. Unit of weight (=200 mgm) used in the sale of diomonds. Also a unit of *expressing the composition of gold, e.g.*, 14 carat gold contains 14 parts of pure gold in 24 parts of the mixture.

Catalysis. The action of substances in changing the rate at which a chemical reaction proceeds.

Catalyst or Catalytic Agent. A substance which by its mere presence alters the rate of a chemical reaction without itself being permanently changed.

Cathode. The negative electrode.

Cathode Rays. A stream of negatively charged electrons.

Cation. Positively charged ion which moves towards the cathode during electrolysis.

Chemical Change. A change in which new substances with different properties are formed.

Chemical Action. A chemical change in which two or more substances are involved.

Chemical Equation. The shorthand method of expressing a chemical reaction with the help of formulae. It is both a qualitative and a quantitative expression.

Chemistry. The exact science dealing with the changes in the composition of matter and our attempts to control or modify such changes.

Colloids Substances with particle size intermediate between the size of molecules and the particles in suspension.

Combining Weights. The proportions by weight in which elements combine with each other to form compounds.

Combustion. Any chemical action producing noticeable light and heat.

Compound. A substance composed of two or more elements combined in unvarying proportions.

Concentration. The quantity of a substance, expressed in weight, gram moles or gram equivalents per unit volume.

Cosmetics. Substances used for external applications to beautify or improve complexion, skin or hair.

Coulomb. The quantity of electricity which is transferred by one ampere current in one second or which deposits 0·001118 gm. of silver.

Covalency. The property by which linkages are set up by mutual sharing of electrons.

Crystal. Solid in which the atoms, ions or molecules of a substance are arranged in a definite orderly pattern.

Decomposition. The process of breaking up of a complex substance into simpler ones.

Degree of Dissociation. Fraction of the total number of molecules dissociated.

Dehydrating Agent. A substance which removes water from another substance.

Deliquescent Substance. A substance which takes moisture from the air to become wet.

Density. Mass per unit volume.

Destructive Distillation. Distillation during which the original compound decomposes to give new products.

Deodorant. Substance used to prevent or mask odours.

Depilatory. A chemical used to remove hair from skin.

Deuterium. Heavy hydrogen, an isotope with atomic weight=2.

Distillation. Process of vaporising a liquid and condensing the vapour produced.

Double Salt. A salt containing two basic radicals combined with one acid radical or *vice versa.*

Dry Ice.– Solid carbon dioxide.

Ductility. Property of metals or their alloys to be drawn into wires.

Effervescence. A brisk escape of gases from a liquid or solution.

Efflorescent. The property of losing water of crystallization by a hydrate on exposure to air.

Electrode. A pole in an electric cell.

Electrolysis. The process of decomposition of an electrolyte by means of an electric current.

Electrolytic Dissociation. The process of splitting up of the solution of an electrolyte to form positive and negative ions.

Electron. The unit of negative charge of electricity and having a mass—1/1845 that of the proton.

Element. A substance which has not been broken up into simpler substances.

Emulsion. A colloidal dispersion of one liquid in another.

Endothermic Reaction. A chemical reaction which proceeds with absorption of heat.

Energy. The capacity of doing work.

Equilibrium (Chemical). A chemical state in which the two opposing reactions in a reversible reaction proceed at equal velocities so that the concentrations of various constituents remain constant.

Equivalent Weight. The number of parts by weight of a substance which combine with or displace directly or indirectly 1·008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine.

Evaporation. Change of liquid to vapour.

Exothermic Reaction. A reaction which proceeds with an evolution of heat.

Faraday. 96,500 coulombs, the quantity of electricity which liberates one gm. equivalent of an ion.

Fermentation. Slow decomposition of organic compounds brought about by living organisms or enzymes.

Fission. Breaking up of complex atomic nuclei into simpler ones.

Fixation of Nitrogen. Conversion of free atmospheric nitrogen into useful compounds.

Fixing. Removal of unchanged sensitive emulsion from sensitive plate with hypo—a process in photography.

Flux. The material added to the ore during smelting. It combines with a portion of the impurities to form slag.

Formula. Symbolic expression for a molecule.

Fractional Distillation. The process of separating by distillation two or more liquids having different boiling points.

Fuel. Any combustible substance which may be burnt to supply heat energy with the production of excessively objectionable by-products.

Fusion. The process of melting a solid.

Galvanizing. The process of coating iron with zinc.

Gamma Rays. Electromagnetic waves with high penetrating power, given off by a radioactive substance.

Gangue. Rocky matter that is not a part of the ore.

Germicide. A compound which kills harmful micro-organisms.

Gram Molecular Weight. The mass in grams of a substance numerically equal to its molecular weight.

Halogen. The name applied to salt forming non-metals belonging to the chlorine family of elements.

Hard Water. Water containing dissolved calcium or magnesium salts which precipitate or curdle soap.

Heat of Combustion. The quantity of heat evolved during the complete combustion of a gram molecule of the substance.

Heat of Formation. The quantity of heat evolved or absorbed during the formation of a gram molecule of a compound from its elements.

Heat of Neutralization. The quantity of heat liberated when a gram equivalent of an acid completely neutralizes a gram equivalent of base in dilute solution.

Heat of Reaction. The quantity of heat evolved or absorbed during the chemical change as indicated by chemical equation.

Heat of Solution. The quantity of heat evolved or absorbed when a gram molecule of the substance is dissolved in excess of the solvent.

Heavy Water. Deuterium oxide written as D_2O, or $H^2{}_2O$.

Hydrate. A crystalline substance containing water of crystallization.

Hydride. A binary compound of an element with hydrogen.

Hydrocarbons. Compounds of carbon and hydrogen only.

Hydrolysis. The chemical reaction of a salt with water to form an acid and a base of unequal strengths—reverse of neutralization.

Hypothesis. A scientific guess used to explain scientific phenomena.

Ignition Temperature. The lowest temperature at which a substance catches fire and continues to burn in air.

Indicator. A substance used to indicate the exact stage at which the chemical reaction involved in a titration is just complete.

Insecticide. A chemical substance used to kill insects.

Ion. An atom or a radical carrying an electrical charge due to loss or gain of electrons.

Ionization. The process of splitting up an electrolyte into ions in solution.

Isobars. Two atoms having the same atomic weight but different atomic numbers.

Isomerism. The condition where two or more molecules are made up of the same number and kind of atoms but differ in their structural formulae.

Isotopes. Two or more atoms of the same element, having the same atomic number but different atomic weights.

Kindling Temperature. See Ignition Temperature.

Lake. The combination of a dye absorbed in a mordant in indirect dyeing.

Laws. The generalization which sum up in themselves a multitude of facts based on laboratory experiments.

Malleability. The property of many metals and alloys of being hammered into thin sheets.

Matter. Anything that occupies space and has weight.

Metallurgy. The process of extraction of a metal from its ore.

generally city.

Mixture. A physical combination of two or more substances.

Molality. The strength of a solution expressed in terms of gram moles of the solute per 1,000 grams of the solvent.

Molarity. The strength of a solution expressed in terms of gram moles of the solute per litre of the solution.

Mole. The weight of a substance in grams, numerically equal to its molecular weight.

Molecular Volume. The volume occupied by a gram-mole of the substance.

Molecular Weight. The sum-total of the atomic weights for all the atoms that make up a molecule of a substance.

Molecule. The smallest particle of a substance which is capable of independent existence and has all the properties of the substance.

Monobasic Acid. An acid having one replaceable hydrogen atom in each molecule, *e.g.*, HCl.

Mordant. Substance used in dyeing to fix a dye on cloth; it is usually an insoluble metallic hydroxide.

Nascent. (Newly freed or new-born). The term applied to a gas that has just been released from chemical union, *e.g.*, nascent hydrogen.

Neutralization. The union of hydrogen ions of an acid with hydroxyl ions of a base to form water.

Neutron. A nuclear atomic particle having mass equal to that of a hydrogen atom and carrying no electric charge.

Non-electrolyte. A substance, the solution of which does not conduct electric current and is not decomposed by it.

Non-metal. An element which forms an acidic oxide.

Normal Salt. A salt formed by the complete neutralization of an acid by a base.

Normal Solution. A solution containing one gram-equivalent weight of the solute per litre.

Nucleus. The central dense and positively charged part of an atom containing protons and neutrons.

Occlusion. Adsorption of gases by a metal.

Octet. The term applied to a group of eight electrons.

Ore. The mineral from which a metal can be profitably extracted.

Osmosis. The movement of a solvent through a semi-permeable membrane from a less concentrated solution into a more concentrated solution.

Osmotic Pressure. Pressure exerted by the solute particles and responsible for osmosis.

Oxidation. A chemical change involving loss of electrons.

Oxide. A binary compound of an element with oxygen.

Oxidizing Agent. A substance which brings about oxidation.

Photosynthesis. Absorption of carbon dioxide by plants in presence of chlorophyll and sunlight to produce glucose, starch and cellulose.

Physical Change. A change involving change in properties only, not in composition.

Precipitate. An insoluble solid which separates as a result of chemical reaction between two or more solutions.

Properties. The characteristics of a substance by which it is recognised.

Proton. A nuclear atomic particle having a mass equal to that of the hydrogen atom and carrying a unit positive charge.

Radical. An atom or a group of atoms forming part of a compound and behaving like a single atom in a chemical change.

Radioactivity. The process of spontaneous disintegration of the atomic nucleus to give alpha, beta and gamma rays.

Rayon. A synthetic fibre resembling natural silk to some extent and derived from cellulose (wood, paper, etc.)

Reducing Agent. A substance which brings about reduction by supplying electrons.

Reduction. A chemical reaction involving gain of electrons.

Reversible Reaction. A reaction in which the [illegible] interact under a different set of conditions to re-form [illegible] substances.

Salt. A compound whose aqueous solution [illegible] positive ion other than H^+ and negative ion other than [illegible]

Saturated Solution. A solution containing as [illegible] solute as it can retain, at a given temperature.

Slag. Product of combination of flux and [illegible] in the ore in metallurgy.

Smelting. Reduction of oxide obtained by [illegible] nation of the [illegible]

Soap. [illegible]

Solubilit [illegible] of an electrolyte.

Solute. The constituent of a solution which [illegible]

[illegible]

Solvent. The constituent of a solution [illegible] nuous medium.

[illegible] phere or 760 mm. pressure).

Sublimation. The process of [illegible] gaseous state and *vice versa* [illegible]

Super-saturated Solution. [illegible] the solute than a saturated [illegible] temperature.

Symbol. An abbreviation [illegible] definite weight of it.

Synthesis. The building [illegible] simpler ones.

Tempering. A regulated [illegible] steel, into required state of [illegible]

Theory. An explanation [illegible] by sufficient evidence but [illegible]

Tincture. A solution [illegible]

Titration. The [illegible] burette to a known volume [illegible] to complete the chemical [illegible]

Transmutation. [illegible]

Valency. The [illegible] lend, borrow or share.

Vapour Density. [illegible] with that of hydrogen.

Welding. The [illegible] pressure.

Zeolite. [illegible]

Appendix VIII

INTERNATIONAL ATOMIC WEIGHTS*

(Based on carbon-12=12)

*(The more important elements are printed in **bold** type. Atomic weights marked* are approximate).*

Name of element	Symbol	Atomic number	Atomic weight	Name of element	Symbol	Atomic number	Atomic weight
Actinum ...	Ac	89	227·0*	**Mercury**	Hg	80	200·59
Aluminium...	Al	13	26·98	Molybdenum..	Mo	42	95·94
Americium...	Am	95	243·0*	Neodymium...	Nd	60	144·24
Antimony ...	Sb	51	121·75	Neon......... ..	Ne	10	20·183
Argon	Ar	18	39·948	Neptunium	Np	93	237*
Arsenic......	As	38	74·92	**Nickel**	Ni	28	58·71
Astatine.. ...	At	85	210·0*	Niobium........	Nb	41	92·91
Barium	Ba	56	137·34	**Nitrogen**........	N	7	14·007
Berkelium ..	Bk	97	249*	Nobelium.......	No	102	254*
Beryllium ..	Be	4	9·012	Osmium.........	Os	76	190·2
Bismuth	Bi	83	208·91	**Oxygen**.	O	8	15·999
Boron...... ..	B	5	10·81	Palladium.......	Pd	46	106·4
Bromine	Br	35	79·81	**Phosphorus**....	P	15	30·974
Cadmium ..	Cd	48	112·40	Platinum........	Pt	78	195·09
Caesium	Cs	55	132·91	Plutonium.. ...	Pu	94	224*
Calcium......	Ca	20	40·08	Polonium	Po	84	210*
Californium	Cf	98	245*	**Potassium**	K	19	39·102
Carbon......	C	6	12·011	Praseodimium	Pr	59	140·907
Cerium.. ...	Ce	58	140·12	Promethium ..	Pm	61	145*
Chlorine.....	Cl	17	35·453	Protactinium...	Pa	91	231*
Chromium...	Cr	24	51·996	Radium	Ra	88	226*
Cobalt.	Co	27	58·03	Radon..........	Rn	86	222*
Copper......	Cu	29	63·54	Rhenium........	Re	75	186·2
Curium.......	Cm	96	245*	Rhodium..... ..	Rh	45	102·905
Drysprosium.	Dy	66	162·50	Rubidium..... ..	Rb	37	85·47
Einsteinium ..	Es	99	254*	Ruthenium......	Ru	44	101·07
Erbium......	Er	68	167·26	Samarium	Sm	62	150·35
Europium...	Eu	63	151·96	Scandium......	Sc	21	44·956
Fluorine.......	F	9	18·998	Selenium........	Se	34	72·96
Fermium....	Fm	100	253	**Silicon**	Si	14	28·086
Francium...	Fr	87	223*	**Silver**...........	Ag	47	107·870
Gadolinium..	Gd	64	157·25	**Sodium**.........	Na	11	22·990
Gallium	Ga	31	69·72	**Strontium**......	Sr	38	87·62
Germanium	Ge	32	72·59	**Sulphur**...	S	16	32·064
Gold... ..	Au	79	196·967	Tantalum.......	Ta	73	180·948
Hafnium	Hf	72	178·49	Technetium ...	Tc	43	99*
Helium	He	2	4·003	Tellurium......	Te	52	127·60
Holmium...	Ho	67	164·93	Terbium........	Tb	65	158·924
Hdyrogen...	H	1	1·008	Thallium	Tl	81	204·37
Indium......	In	49	114·82	Thorium.....	Th	90	232·038
Iodine........	I	53	126·92	Thulium.......	Tm	69	168·934
Iridium.......	Ir	77	192·2	**Tin**...........	Sn	50	118·69
Iron.....	Fe	26	55·85	Titanium......	Ti	22	47·90
Krypton......	Kr	36	83·80	**Tungsten**......	W	74	183·85
Lanthanum	La	57	138·91	Uranium.......	U	92	238·03
Lawrencium	Lw	103	257*	Vanadium.....	V	23	50·942
Lead.........	Pb	82	207·19	Xenon....... ...	Xe	54	131·3
Lithium	Li	3	6·94	Yetterbium.....	Yb	70	173·04
Lutetium....	Lu	71	174·97	Yttrium.........	Y	39	88·905
Magnesium.	Mg	12	24·31	**Zinc**....... ...	Zn	30	65·37
Manganese	Mn	25	54·94	Zirconium.....	Zr	40	91·22
Mendelevium	Md	101	256				

Parenthetical names refer to radioactive elements; the mass number (not the atomic weight) of the isotope with largest half-life is usually given.

**Latest values recommended by the International Union of Pure and Applied Chemistry, 1961.*

Appendix IX

USEFUL TABLES

TABLE I—METRIC-ENGLISH EQUIVALENTS

1 inch	= 2·54 cm.	1 metre	= 39·37 inches
1 ounce	= 28·35 gm.	1 litre	= 1·057 liquid quarts
1 pound	= 453·36 gm.	1 kgm.	= 2·235 pounds.

TABLE II—THERMOMETER CONVERSION TABLE

$$\frac{C}{5}=\frac{F-32}{9} \text{ and } A=C+273$$

Where C = temperature on the Centigrade scale,
F = temperature on the Fahrenheit scale,
and A = temperature on the absolute scale.

TABLE III—AQUEOUS TENSION IN MILLIMETRES OF MERCURY

Temp. °C	Pressure mm.	Temp °C	Pressure mm	Temp. °C	Pressure mm.
−1	4·3	21	18·7	35	42·2
0	4·6	22	19·8	40	55·3
5	6·5	23	21·1	50	92·3
10	9·2	24	22·4	60	149·4
15	12·8	25	23·8	70	233·7
16	13·6	26	25·2	80	355·1
17	14·5	27	26·7	90	525·8
18	15·5	28	28·3	100	760·0
19	16·5	29	30·0		
20	17·5	30	31·8		

TABLE IV—SOME USEFUL VALUES

One gallon water at 62°F weighs 10 pounds
One pound equals 7,000 grains or 453·6 grams
One cup holds about 237 ml of a liquid
One teaspoon holds about 5 ml. and one tablespoon [illegible]
One ordinary test tube holds about 25 ml
Twenty drops make 1 ml

TABLE V—SOME CONVERSIONS

To change	To	Multiply by	To change	[illegible]	[illegible]
Yards	Metres	0·9144	Q[illegible]	[illegible]	[illegible]
Metres	Yards	1·0944	Ga[illegible]	[illegible]	[illegible]
Metres	Inches	39·37	[illegible]	[illegible]	[illegible]
Inches	Centigrades	2·54	[illegible]	[illegible]	[illegible]
Centimetres	Inches	0·3[illegible]	[illegible]	[illegible]	[illegible]

Appendix X

USE OF LOGARITHMS

Use of logarithms greatly facilitates the evaluation of expressions involving multiplication, division, taking of powers and extractions of roots. The way of doing this will be briefly explained here.

Definition : Log x means a number y such that $10^y = x$.

Thus $\log x = y$ is equivalent to $x = 10^y$.

Also then x is called the anitlog of y.

Laws of Logarithms :

(i) $\log xy = \log x + \log y$, (ii) $\log \frac{x}{y} = \log x - \log y$,

(iii) $\log x^n = n \log x$ where n may be integer or fraction.

Logarithmic tables giving logarithms of numbers have been calculated by mathematicians and are available for ready reference. We shall now explain the manner of using the logarithmic tables for writing log of any given number.

Log x, like any other number, consists of two parts, an integral part and a decimal part. Now $\log x$ is positive or negative according as x, is greater than one or less than one. It has been found convenient always to so write $\log x$ that the decimal part appears positive. Thus, for example, if $\log x = -2{\cdot}3213$, we shall write

$$\begin{aligned} -2{\cdot}3213 &= -2 - {\cdot}3213 + 1 - 1 \\ &= -3 + 1 - {\cdot}3213 = -3 + {\cdot}6787 \\ &= \bar{3}{\cdot}6787 \end{aligned}$$

Here $\bar{3}{\cdot}6787$ means $-3 + {\cdot}6787$.

Mantissa. Decimal part of $\log x$, after it has been expressed as a positive expression, is called *Mantissa.*

Characteristic. Integral part of $\log x$, after the decimal part of $\log x$ has been expressed as a positive expression, is called *Characteristic.*

Determination of characteristic. Reference to log tables is not required for this purpose.

If x is greater than one, then the characteristic of $\log x$ is positive and one less than the number of digits in the integral part of x.

If x is less than one so that x begins with decimal point, then the characteristic is negative and is $\overline{a+1}$ if the number of zeros immediately following the decimal point in x is a.

Thus the characteristic of log $25{\cdot}72$ is $2-1=1$ and the characteristic of log ${\cdot}0035$ is $\overline{2+1} = \bar{3}$.

Determination of Mantissa. Mantissa of $\log x$ does not depend upon the position of the decimal point.

To find mantissa, proceed as follows :

(*i*) Remove the decimal point in x.

(*ii*) Remove the zeros occurring in the beginning and in the end. We now suppose that we are left with a figure consisting of four digits, *e.g.*, 2453.

(*iii*) Put one comma after the first two digits and other after *three digits* counting from the left thus 24, 5, 3.

(*iv*) Run down the first vertical column and stop at 24.

(*v*) Run along the first horizontal row and stop at 5.

(*vi*) Read the number standing at the intersection of the row headed by 24 and the column headed by 5. This number is

3892.

(*vii*) Run along the first row in difference columns and stop at 3.

(*viii*) Read the number standing at the intersection of the row headed by 24 and the difference column headed by 3. The number is

5.

(*ix*) Add this number to 3892, when we get 3897.

This is the required mantissa.

Antilogarithms. Def If $\log x=y$, we *say that x is the antilog of y*. Determination of antilogarithms is *done with the help* of Antilogarithmic tables in the manner *to be now explained.*

(*i*) Ignoring the characteristic put down *one comma two* places after the decimal and another comma *three places after the* decimal. Thus if we have to find the *antilog of* $\bar{2}$·2563 *and* of 2·2563 then, ignoring $\bar{2}$ and 2 we write as *follows :*

25, 6, 3.

(*ii*) Now run down the first vertical column and *stop at* ·25.

(*iii*) Run along the first horizontal line and *stop at* 6.

(*iv*) Read the figure at the intersection of the row *headed by* ·25 and column headed by 6. This figure is

1803.

(*v*) Again run along the difference column and stop at 3 and read the figure at the intersection of the row headed by ·25 and difference column headed by 3. This figure is

1.

(*vi*) Add this figure to the one obtained before *so as to obtain*

1804.

(*vii*) Now we have to place the decimal point suitably. This depends upon the given characteristic. If the characteristic is positive and is a, we place the decimal point after $(a+1)$ *figures*. Thus when the characteristic is 2, we put decimal point after 3 figures. Thus antilog of 2·2563 is 180·4. If the characteristic is negative (say$=a$), we place $(a-1)$ zeros before the result obtained and then put down the decimal point. Thus antilog of $\bar{2}$·2563 is ·01804.

(*Continued on page 2·462*)

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Δ_m +	1 (ADD)	2	3	4	5	6	7	8	9
	·6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	9	1	2	3	4	4	5	6	7	8
	·7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	8	1	2	2	3	4	5	6	6	7
	·7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	8	1	2	2	3	4	5	6	6	7
	·7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	8	1	2	2	3	4	5	6	6	7
	·7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	8	1	2	2	3	4	5	6	6	7
	·7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	8	1	2	2	3	4	5	6	6	7
	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	8	1	2	2	3	4	5	6	6	7
7	·7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	8	1	2	2	3	4	5	6	6	7
8	·7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	8	1	2	2	3	4	5	6	6	7
9	·7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	7	1	1	2	3	4	4	5	6	6
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	7	1	1	2	3	4	4	5	6	6
61	·7853	7860	7868	7875	7882	7889	7895	7903	7910	7917	7	1	1	2	3	4	4	5	6	6
62	·7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	7	1	1	2	3	3	4	5	6	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	7	1	1	2	3	3	4	5	6	6
65	·8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	7	1	1	2	3	3	4	5	6	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	7	1	1	2	3	3	4	5	6	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	6	1	1	2	2	3	4	4	5	5
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	6	1	1	2	2	3	4	4	5	5
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	6	1	1	2	2	3	4	4	5	5
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	6	1	1	2	2	3	4	4	5	5
										8567	6	1	1	2	2	3	4	4	5	5
										8627	6	1	1	2	2	3	4	4	5	5
										8686	6	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	[illegible]			8745	6	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	6	1	1	2	3	3	4	4	5	5
76	·8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	6	1	1	2	2	3	4	4	5	5
										8915	6	1	1	2	2	3	4	4	5	5
										8971	6	1	1	2	2	3	4	4	5	5
										9025	6	1	1	2	2	3	4	4	5	5
80	·9031	9036	9042	9047	9053	9058	[illegible]			9079	5	1	1	2	2	3	3	4	4	5
81	·9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	5	1	1	2	2	3	3	4	4	5
82	·9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	5	1	1	2	2	3	3	4	4	5
83	·9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	5	1	1	2	2	3	3	4	4	5
84	·9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	5	1	1	2	2	3	3	4	4	5
85	·9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	5	1	1	2	2	3	3	4	4	5
86	·9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	5	1	1	2	2	3	3	4	4	5
								9430	9435	9440	5	0	1	1	2	2	3	3	4	4
								9479	9484	9489	5	0	1	1	2	2	3	3	4	4
								9528	9533	9538	5	0	1	1	2	2	3	3	4	4
90	·9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	5	0	1	1	2	2	3	3	4	4
91	·9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	5	0	1	1	2	2	3	3	4	4
92	·9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	5	0	1	1	2	2	3	3	4	4
93	·9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	5	0	1	1	2	2	3	3	4	4
94	·9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	5	0	1	1	2	2	3	3	4	4
95	·9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	5	0	1	1	2	2	3	3	4	4
96	·9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	4	0	1	1	2	2	2	3	3	4
97	·9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	4	0	1	1	2	2	2	3	3	4
98	·9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	4	0	1	1	2	2	2	3	3	4
99	·9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	4	0	1	1	2	2	2	3	3	4

ANTILOGARITHMS

x	0	1	2	3	4	5	6	7	8	9	Δm +	1	2	3	4	5	6	7	8	9
												ADD								
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	2	0	0	1	1	1	1	1	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	2	0	0	1	1	1	1	1	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	2	0	0	1	1	1	1	1	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	2	0	0	1	1	1	1	1	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	3	0	1	1	1	1	2	2	2	3
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	3	0	1	1	1	1	2	2	2	3
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	3	0	1	1	1	1	2	2	2	3
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	3	0	1	1	1	1	2	2	2	3
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	3	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	3	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	3	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	3	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	3	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	3	0	1	1	1	2	2	2	2	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	3	0	1	1	1	2	2	2	2	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	3	0	1	1	1	2	2	2	2	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	3	0	1	1	1	2	2	2	2	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	4	0	1	1	2	2	2	3	3	4
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	4	0	1	1	2	2	2	3	3	4
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	4	0	1	1	2	2	2	3	3	4
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	4	0	1	1	2	2	2	3	3	4
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	4	0	1	1	2	2	2	3	3	4
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	4	0	1	1	2	2	2	3	3	4
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	4	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	4	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	4	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	4	0	1	1	2	2	2	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	4	0	1	1	2	2	2	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	4	0	1	1	2	2	2	3	3	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	4	0	1	1	2	2	2	3	3	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	5	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	5	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	5	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	5	1	1	2	2	3	3	4	4	5
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	5	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	5	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	5	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	6	1	1	2	2	3	4	4	5	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	6	1	1	2	2	3	4	4	5	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	6	1	1	2	2	3	4	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	6	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	6	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	6	1	1	2	2	3	4	4	5	5
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	6	1	1	2	2	3	4	4	5	5
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	6	1	1	2	2	3	4	4	5	5
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	7	1	1	2	3	3	4	5	6	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	7	1	1	2	3	3	4	5	6	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	7	1	1	2	3	3	4	5	6	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	7	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	7	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

x	0	1	2	3	4	5	6	7	8	9	Δm +	1	2	3	4	5	6	7	8	9
												ADD								
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	7	1	1	2	3	4	4	5	6	6
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	8	1	2	2	3	4	5	6	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	8	1	2	2	3	4	5	6	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	8	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	8	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	8	1	2	2	3	4	5	6	6	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	8	1	2	2	3	4	5	6	6	7
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	9	1	2	3	4	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	9	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	9	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	9	1	2	3	4	5	5	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	10	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	10	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	10	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	10	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	10	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	11	1	2	3	4	5	7	8	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	11	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	11	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	11	1	2	3	4	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	12	1	2	4	5	6	7	8	10	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	12	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	12	1	2	4	5	6	7	8	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	12	1	2	4	5	6	7	8	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	13	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	13	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	13	1	3	4	5	7	8	9	10	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	14	1	3	4	6	7	8	10	11	13
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	14	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	14	1	3	4	6	7	8	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	15	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6545	6561	6577	6592	15	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	15	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	16	2	3	5	6	8	10	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	16	2	3	5	6	8	10	11	13	14
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	16	2	3	5	6	8	10	11	13	14
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	17	2	3	5	7	8	10	12	14	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	17	2	3	5	7	9	10	12	14	15
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	18	2	4	5	7	9	11	13	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	18	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	18	2	4	5	7	9	11	13	14	16
·91	8128	8147	8165	8185	8204	8222	8241	8260	8279	8299	19	2	4	6	8	10	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	19	2	4	6	8	10	11	13	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	20	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	20	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9035	9057	9078	9099	21	2	4	6	8	11	13	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	21	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	22	2	4	7	9	11	13	15	18	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	22	2	4	7	9	11	13	15	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	23	2	5	7	9	11	14	16	18	21

(Continued from page 2·457)

Example 1. Simplify : $\frac{432{\cdot}6 \times {\cdot}0956}{2{\cdot}678 + 39{\cdot}54}$.

Let the expression be $= x$

Then $\log x = \log 432{\cdot}6 + \log {\cdot}0956 - \log 2{\cdot}678 - \log 39{\cdot}54$

$= 2{\cdot}6361 + \bar{2}{\cdot}9850 - 0{\cdot}4278 - 1{\cdot}5970$

$= \bar{1}{\cdot}5918$

or $x = \text{Antilog } \bar{1}{\cdot}5918 = {\cdot}3906.$

Example 2. Simplify : $\sqrt{68{\cdot}96} \times \sqrt[3]{86{\cdot}25}$.

Let the expression be $= x$

Then $\log x = \frac{1}{2} \log 68{\cdot}96 + \frac{1}{3} \log 86{\cdot}25.$

$= \frac{1}{2} + 1{\cdot}8386 + \frac{1}{3} \times 1{\cdot}9358.$

$= {\cdot}9193 + {\cdot}6453 = 1{\cdot}5646$

or $x = \text{Antilog } 1{\cdot}5646 = 36{\cdot}69.$

Example 3. Simplify : $\sqrt[3]{{\cdot}0654} \times (5{\cdot}439)^2$.

Let the expression be $= x$

Then $\log x = \frac{1}{3} \log {\cdot}0654 + 2 \log 5{\cdot}439$

$= \frac{1}{3} \times \bar{2}{\cdot}8156 + 2 \times {\cdot}7355$

$= \frac{1}{3} \times (-1{\cdot}1844) + 1{\cdot}4710$

$[\because \bar{2}{\cdot}8156 = -2 + {\cdot}8156]$

$= -{\cdot}3948 + 1{\cdot}4710 = 1{\cdot}0762$

or $x = \text{Antilog } 1{\cdot}0762 = 11{\cdot}92.$

Example 4. Simplify : $\frac{66{\cdot}72 \times 7{\cdot}539}{\sqrt{88{\cdot}6} \times {\cdot}05}$.

Let the expression be $= x$

Then $\log x = \log 66{\cdot}72 + \log 7{\cdot}539 - \frac{1}{2} \log 88{\cdot}6 - \log {\cdot}05$

$= 1{\cdot}8242 - 0{\cdot}8773 - \frac{1}{2}(1{\cdot}9474) - \bar{2}{\cdot}6990$

$= 2{\cdot}7015 - 0{\cdot}9737 - \bar{2}{\cdot}6990$

$= 2{\cdot}7015 - \bar{1}{\cdot}6727 = 3{\cdot}0288$

or $x = \text{Antilog } 3{\cdot}0288 = 1069.$

Example 5. Simplify : $\frac{456{\cdot}2 \times \sqrt{58{\cdot}1} \times {\cdot}005}{(2{\cdot}34)^2 \times 27{\cdot}3}$.

Let the expression be $= x$

Then $\log x = \log 456{\cdot}2 + \frac{1}{2} \log 58{\cdot}1 + \log {\cdot}005$

$- 2 \log 2{\cdot}34 - \log 27{\cdot}3$

$= 2{\cdot}6592 + \frac{1}{2} \times 1{\cdot}7642 + \bar{3}{\cdot}6990 - 2 \times {\cdot}3692 - 1{\cdot}4362$

$= 2{\cdot}6592 - {\cdot}8821 + \bar{3}{\cdot}6990 - {\cdot}7384 - 1{\cdot}4362 = \bar{1}{\cdot}0657$

$x = \text{Antilog } \bar{1}{\cdot}0657 = {\cdot}1163.$

Note :—Antilog $0{\cdot}0657 = 1{\cdot}163$ Antilog $2{\cdot}0657 = 116{\cdot}3$

" $1{\cdot}0657 = 11{\cdot}63$ " $3{\cdot}0657 = 1163.$

Index

(Numbers refer to pages)